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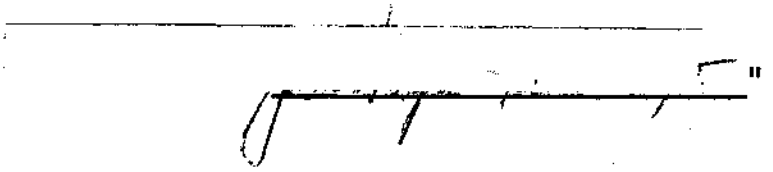

VAPOR-LIQUID EQUILIBRIA IN NITROPARAFFIN-HYDROCARBON SYSTEMS WHICH EXHIBIT PARTIAL MISCIBILITY

A THESIS

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the Faculty of the Graduate Division

By

James Byrd Edwards, II

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VAPOR-LIQUID EQUILIBRIA IN NITROPARAFFIN-HYDROCARBON SYSTEMS WHICH EXHIBIT PARTIAL MISCIBILITY

Approved:

W. T. Ziegler, Chairman

William Meese Newton

Henderson C. Ward

Date Approved by Chairman July 10, 1964

DEDICATION

This work is dedicated to my mother who through her Christian ideals, integrity, training, example, and devotion to her four fatherless children made this work possible. Her self-sacrifice gave them a happy childhood and an education at the expense of her own leisure and thirst for knowledge.

Max Planck ... on problems

The world is teeming with problems. Wherever man looks, he encounters some new problem – in his home life and in his job, in economics and in technology, in the arts and in the sciences. And some problems are very stubborn; they refuse to leave us in peace. They torture our thoughts, sometimes haunting us throughout the day and even robbing us of sleep at night. If by lucky chance we succeed in solving a problem, we experience a sense of deliverance and rejoice over the enrichment of our knowledge. But it is a different story, and highly annoying, to discover after tedious efforts that the problem is incapable of solution – either because there exists no indisputable method of solving it or, because soberly looked at, it is void of meaning – a phantom problem on which our labors and thoughts were wasted. There are a good many such phantom problems – in my opinion, far more than is ordinarily assumed – even in the sciences.

– Scheinprobleme der Wissenschaft, 1947

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TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS iv

LIST OF FIGURES vii

LIST OF TABLES viii

SUMMARY x

NOMENCLATURE AND DEFINITION OF TERMS xxii

Chapter

I. INTRODUCTION TO THE PROBLEM 1

II. EXPERIMENTAL APPARATUS AND MATERIALS USED 13

III. EXPERIMENTAL PROCEDURE 22

IV. DISCUSSION OF RESULTS 25

V. CONCLUSIONS AND RECOMMENDATIONS 40

APPENDICES 43

A. IDENTIFICATION AND DESCRIPTION OF COMMERCIALLY MADE INSTRUMENTS USED IN THIS RESEARCH 44

B. PRESSURE AND TEMPERATURE CONVERSION TABLES 46

C. PHYSICAL PROPERTIES AND PURIFICATION OF MATERIALS 51

D. EXPERIMENTAL VAPOR-LIQUID DATA 55

E. THE REDLICH-KISTER EQUATION 67

F. SUMMARY OF THE RESULTS OF THE THERMODYNAMIC CONSISTENCY TESTS AND THE REDLICH-KISTER LEAST SQUARES FIT TO EXPERIMENTAL VAPOR-LIQUID DATA 71

G. VIRIAL COEFFICIENTS 94

H. THERMODYNAMIC CONSISTENCY TEST 97

BIBLIOGRAPHY 106

VITA 109

LIST OF FIGURES

Figure — Page

1. Diagram of Apparatus Layout 21

2. The Redlich-Kister Constants (Calculated from Mutual Solubility Data) Versus Reciprocal Absolute Temperature . . . 35

3. The Constants of the 4-Constant Redlich-Kister Excess Free Energy Model (Fitted to Vapor-Liquid Equilibrium Data) Versus Reciprocal Absolute Temperature 37

LIST OF TABLES

Table		Page
1.	Summary of the Systems for Which Vapor-Liquid Equilibrium Data Were Measured in this Research	xii
2.	Pressure Correction Factors	48
3.	Results of the Fourth Degree Polynomial Fit to the Thermocouple Calibration Data	49
4.	Constants for the Fourth Degree Orthogonal Polynomial, EMF = EMF(T)	50
5.	Refractive Index of Materials Used in this Research	53
6.	Vapor-Pressures of Pure Chemicals Used in this Research	54
7.	Experimental Binary Vapor-Liquid Equilibrium Data	55
8.	Experimental Binary Vapor-Liquid Equilibrium Data	56
9.	Experimental Binary Vapor-Liquid Equilibrium Data	57
10.	Experimental Binary Vapor-Liquid Equilibrium Data	58
11.	Experimental Binary Vapor-Liquid Equilibrium Data	59
12.	Experimental Binary Vapor-Liquid Equilibrium Data	60
13.	Experimental Binary Vapor-Liquid Equilibrium Data	61
14.	Experimental Binary Vapor-Liquid Equilibrium Data	62
15.	Experimental Binary Vapor-Liquid Equilibrium Data	63
16.	Experimental Ternary Vapor-Liquid Equilibrium Data	64
17.	Second Virial Coefficients and Liquid Molal Volumes Used for Computation for Binary Solutions	96
18.	Summary of the Results of the Thermodynamic Consistency Test Using the Method of Techo	72
19.	Values of the Redlich-Kister Constants Determined by a Least Squares Fit to the Experimental Vapor-Liquid Data	73

20. Closeness of Fit of the Redlich-Kister Model to the Experimental Vapor-Liquid Equilibrium Data 80

21. Comparison of Experimental Mutual Solubility Data with Values Predicted by the Redlich-Kister Fit to Experimental Vapor-Liquid Data 82

22. The Redlich-Kister Constants Calculated from Hwa's Mutual Solubility Data 83

23. Comparison of the 4-Constant Redlich-Kister Equation Fitted by Least Squares to the Experimental Vapor-Liquid Data with the 2-Constant Redlich-Kister Equation Fitted to Experimental Solubility Data 84

24. Values of the 4-Constant Redlich-Kister Constants at Different Temperatures 87

25. Summary of Least Squares Fit of Ternary Redlich-Kister Equation 88

26. Ternary Interaction Constants Obtained by Least Squares Fit to Ternary Redlich-Kister Equation 89

27. Redlich-Kister Calculations Using the 4-Constant Least Squares Redlich-Kister Equation 90

SUMMARY

This research was undertaken to ascertain the applicability of a general equation, which was proposed by Redlich and Kister[1], to the prediction of vapor-liquid phase equilibrium of binary mixtures which exhibit partial miscibility, using only a knowledge of the liquid-liquid phase equilibrium of the mixtures. A second purpose was to determine the applicability of the Redlich-Kister equation to the prediction of vapor-liquid phase equilibrium in partially miscible ternary solutions, using only a knowledge of the equilibrium properties of the constituent binary pairs.

The Redlich-Kister equation was used in this study because of its mathematical flexibility, coupled with the fact that the vapor-liquid data for many systems have been shown to be adequately represented by the Redlich-Kister model for the Gibbs excess free energy[2]. This model is essentially a truncated power series expansion of the Gibbs excess free energy in terms of liquid compositions and undetermined parameters. Although Hala *et al.*[25] have shown that this model can be obtained from the more general Wohl equation by making certain simplifying assumptions, the Redlich-Kister model was originally presented as a power series expansion of the Gibbs excess free energy function in such a way that the higher terms were corrections of the terms of lower order. Partial differentiation of the Redlich-Kister model with respect to the mole numbers yielded a set of equations for the logarithms of the

activity coefficients as functions of the liquid composition and parameters.

A literature survey was made to collect the data for the binary systems. Specifically, the data desired were:

1. Isothermal vapor-liquid equilibrium data below the critical solution temperature for the homogeneous regions (on both sides of the binodal curve) of partially miscible binary solutions.

2. Isothermal vapor-liquid equilibrium data above the critical solution temperature for these binary solutions.

3. Liquid-liquid mutual solubility data for the same binary solutions.

A literature survey was made to collect the data for the ternary system. The data desired were:

1. Isothermal vapor-liquid equilibrium data for a partially miscible ternary system.

2. Isothermal vapor-liquid equilibrium data for the constituent binary systems.

3. Liquid-liquid mutual solubility data for the ternary system.

The desired data were not found for any partially miscible binary system or for any partially miscible ternary system. This finding was substantiated by a similar report[3]. Therefore a decision was made to determine experimentally the desired vapor-liquid equilibrium data for some specific systems for which the mutual solubility data had been previously reported in the literature. The systems chosen were hydrocarbon--nitroethane systems investigated by Hwa[4] and Techo[3]. Hwa

had reported the binary solubility data and Techo had reported the mutual solubility data for the ternary solution chosen for this research.

Table 1 presents a summary of the systems investigated in this research, the temperature at which the vapor-liquid data were measured, the number of experimental data points obtained for each system, and the values Hwa reported for the critical solution temperatures.

Table 1. Summary of the systems for Which Vapor-Liquid Equilibrium Data Were Measured in This Research

Systems	Equilibrium Temperature °C	Critical Solution Temperature °C	Number of Experimental Vapor-Liquid Data Points
normal octane--nitroethane	35.00	41.3	13
2,2,4-trimethylpentane--nitroethane	45.00	29.5	14
2,2,4-trimethylpentane--nitroethane	35.00	29.5	21
2,2,4-trimethylpentane--nitroethane	25.00	29.5	10
normal hexane--nitroethane	45.00	29.3	15
normal hexane--nitroethane	25.00	29.3	13
2-methylpentane--nitroethane	25.00	26.7	13
normal octane--2,2,4-trimethylpentane--nitroethane	35.00	-----	26
nitromethane--benzene	45.00	-----	15

From Table 1 it can be seen that vapor-liquid equilibrium data were measured below the critical solution temperature for each of the

partially miscible systems. Such measurements were confined to the homogeneous liquid concentration range (on both sides of the binodal curve). Vapor-liquid equilibrium measurements were also made above the critical solution temperature for the 2,2,4-trimethylpentane--nitroethane system and the normal hexane--nitroethane system.

The nitromethane--benzene system was investigated using the vapor-liquid equilibrium still built for this research and the results were compared with the data of Brown and Smith[5]. The data from this research and the data of Brown and Smith were both shown to be thermodynamically consistent. Furthermore the equilibrium total pressure and the equilibrium liquid and vapor compositions of both sets of data were found to be in good agreement. Thus an independent check was afforded for the accuracy of the vapor-liquid equilibrium apparatus used in this research.

The equilibrium apparatus used to determine the vapor-liquid equilibrium data consisted of:

1. A flow-type vapor-liquid equilibrium still.
2. A manostat for controlling the pressure.
3. A manometer for measuring the total pressure of the system.
4. A thermocouple for measuring the equilibrium temperature.
5. Analytical instruments for determining the composition.

The equilibrium still was a flow-type still described by Vilim et al.[6]. Unlike most other stills, the flow-type still can be used to measure the vapor-liquid phase equilibrium in systems which exhibit partial miscibility. Since the systems of interest in this research

were partially miscible, the use of most of the other types of stills was excluded. Furthermore, there are indications that prolonged heating of distillation residues of nitroethane at atmospheric pressure has led to violent explosions[7]. Since the equilibrium measurement in the flow-type still is completed in a matter of minutes as compared with some hours for other type stills, the safety viewpoint also influenced the selection of the flow-type still. Insofar as the precision of the instrument is concerned, Vilim et al. showed the results obtained from this type still to be thermodynamically consistent. The results of the present research confirm this observation.

The manostat chosen for this research was a modification of the Williams[8] type manostat. Vilim et al.[6] give the details of the construction. The manostat maintained the pressure constant to within 0.01 mm. Hg.

The manometer was an absolute type U-tube mercury manometer constructed of 19 mm. inside diameter Pyrex glass tubing. The height of the mercury column was measured by comparison with a stainless steel standard meter bar which was located vertically within two seconds of arc and was graduated in 0.1 cm. intervals. The 0.1 cm. subintervals of the meter bar were interpolated to 0.005 cm. by using a cathetometer.

The thermocouple was a copper-constantan couple calibrated against an NBS certified mercury thermometer which was graduated in 0.1°C subintervals. The thermocouple EMF was measured by a Leeds and Northrup type K-3 potentiometer used in conjunction with a Leeds and Northrup type E galvanometer. Vapor pressure measurements made in the

equilibrium still indicated that the probable error in the temperature was 0.02°C.

The compositions were determined by a refractometer and gas chromatographic analysis. The refractive index analysis was reproducible to 0.0005 mole fraction unit. The estimated error in the chromatographic analysis was 0.0005 mole fraction unit for the binary mixtures and 0.002 mole fraction unit for the ternary mixture.

All systems were tested for thermodynamic consistency by using the method described by Techo[3]. Briefly, Techo described his procedure as a method for using electronic digital computers to determine the thermodynamic consistency of isothermal binary vapor-liquid equilibrium data. Two sets of orthogonal polynomials, $P = p(x)$ and $Y = y(x)$, were obtained by fitting the experimental total pressure and vapor composition data as functions of liquid composition according to the method of least squares. For $p(x)$ and $y(x)$ various polynomials ranging in degree from two to the number of experimental data points less one were determined. All of the combinations of the degrees of the fitted polynomials were used to compute the excess chemical potentials which were substituted into the Gibbs-Duhem equation. That combination of polynomials, $P = p(x)$ and $Y = y(x)$, which minimized the Gibbs-Duhem equation was said to characterize the experimental data in the best possible manner with regard to the thermodynamic consistency of the data.

The results of Techo's consistency test indicated that the data for the following systems were thermodynamically consistent:

1. 2,2,4-trimethylpentane--nitroethane at 35.00°C.
2. 2,2,4-trimethylpentane--nitroethane at 45.00°C.
3. Normal octane--nitroethane at 35.00°C.
4. Nitromethane--benzene (Brown and Smith[5]) at 45.00°C.
5. Nitromethane--benzene (this research) at 45.00°C.

The results of the consistency test for the other systems studied in this research indicated an insufficient number of experimental data points for each system. This conclusion was based on the observation that the degrees of the best fitting $p(x)$ or $y(x)$ polynomials for these systems were equal to the maximum possible degree which could be fitted to the number of available points.

Lacking more experimental data for these systems, one is forced to resolve the issue of thermodynamic consistency by some other method. One such method would involve the selection of a thermodynamically consistent model for the excess free energy function, and the evaluation of the parameters of this function by a least squares technique. Then one might reasonably conclude that if the experimental (x, y, P, T) data set were back calculated from the fitted excess free energy model within some arbitrarily prescribed limits of agreement, then the model chosen could be said to represent adequately the experimental data, and furthermore the data could be considered to be thermodynamically consistent. A proof was developed and presented in this research to show that this criterion is in fact a sufficient condition for thermodynamic consistency. It is worthwhile to point out here that this approach to the thermodynamic consistency of vapor-liquid data has

apparently either been overlooked by other investigators, or it has been regarded by them as a not sufficient condition. The method developed in this research has an obvious advantage over the more popular slope or area tests for consistency, namely, it provides a measure of the inconsistency of the data in terms of experimentally measured quantities (x, y, P, T), rather than some other quantities which are not subject to direct measurement (e.g., activity coefficient, excess free energy, chemical potential, slope of chemical potential with respect to composition, etc.).

The use of this method in conjunction with the Redlich-Kister model for the Gibbs excess free energy showed all the data measured in this research to be thermodynamically consistent.

In order to investigate the effect of the number of constants used in the Redlich-Kister model, the 1-, 2-, 3-, 4-, and 5-constant Redlich-Kister models were fitted to the experimental vapor-liquid data by the method of least squares. It was observed that the higher order terms served as corrective terms for the terms of lower order. This was in agreement with the observations of Redlich and Kister. The 4-constant equation agreed with the experimental data with a maximum deviation of ± 0.0005 mole fraction and ± 0.16 mm. Hg. The mutual solubility curve calculated from the 4-constant equation agreed with the values reported by Hwa within 0.002 mole fraction unit. Therefore, the 4-constant model was chosen as an adequate mathematical representation of the data.

The following observations were made from this investigation:

1. The data obtained from the flow-type vapor-liquid equilibrium apparatus constructed for this research were found to be thermodynamically consistent. This conclusion was based on a total of eight sets of binary isothermal vapor-liquid equilibrium data for five binary systems and one set of ternary isothermal data measured in the equilibrium apparatus. Four sets of the binary data were measured below the critical solution temperature.

2. The 4-constant Redlich-Kister binary model for the Gibbs excess free energy was found to adequately represent the vapor-liquid equilibrium data of the binary hydrocarbon--nitroethane systems studied in this research, both above and below the critical solution temperature.

3. The Redlich-Kister ternary model for the Gibbs excess free energy was found to adequately represent the vapor-liquid data in the partially miscible ternary system (normal octane--2,2,4-trimethylpentane--nitroethane) using only the constants of the Redlich-Kister 4-constant model for the constituent binary pairs. The agreement of the fit was 0.002 mole fraction unit and 0.11 mm. Hg.

4. The parameters of the binary Redlich-Kister 2-constant model were calculated below the critical solution temperature from the mutual solubility data of Hwa [4]. Linear relationships were found to exist between these constants and the reciprocal of the absolute temperature below the critical solution temperature. The values of the vapor composition and total pressure calculated from these 2-constant models were found to agree well with the values calculated from the 4-constant

models chosen to represent the experimental vapor-liquid data below the critical solution temperature for the homogeneous liquid concentration range between 0.1 and 0.9 mole fraction. This indicates that, from mutual solubility data only, for the systems studied, the 2-parameter model could be successfully used to obtain values in the homogeneous region of a partially miscible binary system.

5. The linear relationships were extrapolated to temperatures above the critical solution temperature to obtain an estimate of the values of the parameters of the Redlich-Kister 2-constant model at these higher temperatures. The values of the vapor composition and the total pressure calculated from these 2-constant models were found to agree with the values calculated from the 4-constant models chosen to represent the experimental vapor-lqiuid data, provided the temperature was not close to the critical solution temperature. Near the critical solution temperature the agreement was less by an order of magnitude. This indicates that, for partially miscible binary systems, the mathematical models used in this research to describe the homogeneous region below the critical solution temperature can be extrapolated to adequately describe the homogeneous properties above the critical solution temperature.

6. The ternary experimental data were compared with the results calculated from the combination of the 2-constant Redlich-Kister parameters obtained from the mutual solubility data (normal octane) and the parameters estimated from the linear extrapolation (2,2,4-trimethylpentane), assuming the normal octane--2,2,4-trimethylpentane binary

system to be ideal. The calculated results were found to differ from the experimental values by as much as 0.01 mole fraction unit and four mm. Hg.

Based on the results of this work several conclusions were drawn. These conclusions, while applying specifically to the systems studied, are presented in a general form because it is believed that they may have application to other systems as well.

1. Using the Redlich-Kister 2-constant model, it is possible to successfully predict the isothermal vapor-liquid phase equilibria below the critical solution temperature of a binary mixture from liquid-liquid solubility data.

2. Using the Redlich-Kister 2-constant model, it is possible to successfully predict the isothermal vapor-liquid phase equilibria of a binary mixture above the critical solution temperature by extrapolation of the mathematical model used to describe the binary mixture below the critical solution temperature. If the temperature of interest is within a few degrees of the critical solution temperature, such a prediction may be unsatisfactory.

3. Using the Redlich-Kister model, it is possible to successfully predict the isothermal vapor-liquid phase equilibria of a partially miscible ternary mixture using only a knowledge of the equilibrium properties of the constituent binary pairs.

4. A new method was developed for testing the thermodynamic consistency of vapor-liquid equilibrium data. The method uses a criterion which was shown in this research to be a sufficient condition

for thermodynamic consistency. The method has a decided advantage over the more popular slope type and area type tests in that it bases the criterion of consistency directly on the agreement with the experimentally measured (x, y, P, T) data.

NOMENCLATURE AND DEFINITION OF TERMS

In the absence of a universally accepted system of notation for thermodynamic quantities, individual authors have the responsibility of making a choice whenever the existing systems are in conflict. The initiate in the field usually follows the notation of a text from which he has studied or uses standards set up by some professional society. With several exceptions, this paper will follow the notations used by I. Prigogine and R. Defay in their book, Chemical Thermodynamics, translated by D. H. Everett[22].

LIST OF SYMBOLS

a_i	activity of component i
B, B(T)	second virial coefficient in liters/gram-mole
d	symbol for differentiation
e	base of natural logarithms
G^E	Gibbs excess free energy
g^E	Gibbs molar excess free energy
ΔH^M	integral heat of mixing
i	as a subscript refers to a generalized component
j	as a subscript refers to a second generalized component
K	a constant
ln	natural logarithm
log	logarithm to the base 10
n_i	number of moles of component i
P	total pressure of a system
p_i	partial pressure of component i
p_i^o	vapor pressure of pure component i
R	gas constant
R_{12}	equivalent to $2B_{12}(t) - B_{11}(t) - B_{22}(t)$
T	absolute temperature in degrees Kelvin
T_c	critical temperature in degrees Kelvin
T_r	reduced temperature = T/T_c
t	temperature in degrees centigrade

ΔV^E	excess molar volume of mixing
v	molar volume
V_i^o	molar volume of pure liquid component i
x_i	mole fraction of component i

GREEK ALPHABET

γ_i	activity coefficient of component i
∂	symbol for partial differentiation
μ_i^E	excess chemical potential of component i
$\sum$	symbol for summation
(number)	denotes a reference to the bibliography; denotes an equation number. The word "equation" precedes this symbol.

CHAPTER I

INTRODUCTION

The main purpose of undertaking this research was to ascertain the applicability of a general equation, which was proposed by Redlich and Kister[1], to the prediction of vapor-liquid phase equilibrium of binary solutions which exhibit partial miscibility, using only a knowledge of the liquid-liquid phase equilibrium of the mixtures. A second purpose was to ascertain the applicability of the Redlich-Kister equation to the prediction of vapor-liquid phase equilibrium in partially miscible ternary solutions, using only a knowledge of the equilibrium properties of the constituent binary pairs.

The two general concepts which are to be examined in this research were proposed a number of years ago. However, the basic assumptions involved in them were so simple that their validity was harder to believe than to doubt at first presentation. Furthermore, the validity of these concepts has become obscured in a cloud of observations, and hence the basis for promulgating their use has been one of expediency rather than discerning judgement. Such a situation was rather elegantly described by Lucretius in the first century B. C.

> No fact is so simple that it is not harder to believe than to doubt at the first presentation. Equally, there is nothing so mighty or so marvelous that the wonder it evokes does not tend to diminish in time. Take first the pure and undimmed lustre of the sky and all that it enshrines: the stars that roam across its surface, the moon and the surpassing splendor

> of the sunlight. If all these sights were now displayed to mortal view for the first time by a swift unforeseen revelation, what miracle could be recounted greater than this? What would men before the revelation have been less prone to conceive possible? Nothing surely. So marvelous would have been that sight – a sight which no one now, you will admit, thinks worthy of an upward glance into the luminous regions of the sky. So has satiety blunted the appetite of our eyes. Desist, therefore, from thrusting out reasoning from your mind because of its disconcerting novelty. Weigh it, rather, with discerning judgement. Then, if it seems to you true, give in. If it is false, gird yourself to oppose it.

The first purpose of the research deals with the idea of predicting binary vapor-liquid equilibrium data from mutual solubility data, and this idea is certainly not new. Nor is there anything novel about the general idea involved in the second purpose of this research, i.e., predicting ternary properties from a knowledge of the properties of the constituent binary pairs. For example, Robinson and Gilliland[9] and Treybal[10] mention the use of mutual solubility data for binary systems as a basis for calculating binary vapor-liquid equilibrium data, and Treybal[10] and Rowlinson[11] refer to the use of binary equilibrium data to predict the ternary equilibrium relationships. Where, then, is the "disconcerting novelty" of which Lucretius speaks? It is in the applicability of these two general ideas to actual systems which exist in the real physical world. From the viewpoint of the imaginary world of mathematics, these two ideas have certain merit. For example, if one conceded that a particular two-parameter mathematical model exactly described the phase equilibria (both vapor-liquid and liquid-liquid) of a partially miscible binary system, then the methods of Robinson and Gilliland[9] and Treybal[10] show how these two parameters may be evaluated from liquid-liquid mutual solubility data. On the other hand,

if one knew a priori that the phase equilibria of a given partially miscible binary solution were not exactly described by a mathematical model with only two parameters, then mutual solubility data obviously could not give sufficient information to obtain the parameters of this mathematical model, and, therefore, one could not predict exactly the vapor-liquid equilibria from the liquid-liquid equilibria. Similarly, the successful prediction of ternary vapor-liquid equilibrium data from only the equilibrium data for the constituent binary pairs depends on the validity of the assumption that a mathematical model which represents the ternary system is obtainable by some combination of the mathematical models which describe the binary systems.

In other words, the two general ideas which are to be examined in this research were originally considered to have some merit simply because of the tacit assumption that the behavior of certain types of systems found in the real physical world can be described by particular types of models taken from the imaginary world of mathematics. It would seem upon a cursory examination that one could test the validity of the first idea simply by obtaining both mutual solubility data and vapor-liquid data for a partially miscible binary system, and then deciding whether the observations were described by the required type of mathematical model. Likewise, it would seem that the truth of the second idea could be tested by obtaining vapor-liquid data for a partially miscible ternary solution along with the same type of data for the constituent binary pairs, and then deciding whether the prescribed mathematical model described the observed behavior of the particular system.

However, even before one searches the literature for experimental observations, it is well to keep in mind that there are some well-known shortcomings of any mathematical model used to describe a partially miscible binary system, and, keeping in mind the words of Lucretius, it is precisely these shortcomings which would make the two ideas under discussion harder to believe than to doubt. Herington[12], for example, showed that it is necessary for the activity coefficient, γ_i, to vary inversely with the liquid composition, x_i, in the two-phase liquid-liquid region of a partially miscible binary solution. This necessary relationship, expressed mathematically as Equation (1), arises because of the requirement that the phases are in fact in equilibrium.

$$\gamma_i = \frac{K}{x_i} \tag{1}$$

Furthermore, the Redlich-Kister equation, which is the particular mathematical model used in this research, never reduces identically to Equation (1) over any finite composition range. Thus, any attempt to describe the behavior of any partially miscible system by the Redlich-Kister equation seems doomed to failure even before one tries to obtain experimental data in order to determine the validity of the model. But this brings up a question of even more fundamental significance. Has the behavior of any system in the real physical world been shown to be exactly described by a mathematical model? Three words in this question, namely, "behavior," "describe," and "exactly," need further amplification. By "behavior" is meant the action or reaction of a system in

relation to its environment. By "describe" it is meant that the value of the range of the mathematical function must be in accord with the behavior of the system for every value of the applicable mathematical domain. Thus, if one allows the mathematical domain to consist of a continuous interval, then the model is said to describe the real physical system if and only if the model predicts the behavior of the system for all possible domain values for which the real physical system exists, i.e., the model must accurately interpolate between discrete sets of observations (data). The word "exactly" will be taken to mean that the numbers calculated from the mathematical model have no error associated with them.

Now, the only way one has of relating a mathematical model to the behavior of any system of the real physical world is by means of observed values of physical quantities. The observed values are usually referred to as experimental data. One can never relate a mathematical model directly to the behavior of a real physical system without this transitional device, called "experimental data." The process involves observing a system to obtain the experimental data, and then making computations to determine the applicable mathematical model. Values which are calculated from the model are then compared with their corresponding observed (experimental) values. If the calculated and experimental results agree within some arbitrary limits, the model is said to describe the system insofar as the discrete set of observations are concerned. But one is still not in the position to speak with certainty of the accuracy of the values calculated from such a

model if domain values are involved which are not contained within the discrete set of observations.

If the experimental data have inherent error, no matter how small, any mathematical model which exactly describes the set of experimental data cannot exactly describe the behavior of the system, except by a most fortuitous coincidence. Likewise, if a mathematical model does not exactly describe a set of experimental data, one cannot say for a certainty that the model does not describe the behavior of the system under consideration. Few will assert that any observation is without error. Therefore, one is forced to concede that at the present time there is no system in the real physical world whose behavior has been shown to be exactly described by a mathematical model.

Having conceded the point, one then asks another question which is more realistic. If experimental data for a system have some error inherent in them, is it possible to approximate the behavior of the system by a mathematical model which represents the data? The answer to this question is obviously yes, since the word "approximate" is certainly open to a wide range of interpretations.

Many such approximations involve extremely careful and accurate work. The key to the issue lies in the type of mathematical model chosen and the accuracy of the experimental data. For example, if a power series expansion is chosen which can be shown to approximate as closely as one pleases any continuous function, provided sufficient terms are taken, it would obviously be expected that any set of discrete data points could be described with any arbitrary accuracy by

such a model. Hence, even though there is the evidence of Herington[12] to cause us to look dimly on any hope of success from the standpoint of absolute accuracy, there is certainly hope that some types of mathematical models will approximate the data to the desired degree of accuracy.

The work of other investigators may now be examined. Techo[3] conducted a comprehensive survey of the literature in which Chemical Abstracts (1947-1959) and five other secondary reference sources were examined for isothermal binary and ternary vapor-liquid data in partially miscible systems. During the course of the present investigation a similar search was made using Chemical Abstracts (1907-1961). Specifically, the binary data desired were:

1. Isothermal vapor-liquid equilibrium data below the critical solution temperature for the homogeneous regions (on both sides of the binodal curve) of partially miscible binary solutions.

2. Isothermal vapor-liquid equilibrium data above the critical solution temperature for these binary solutions.

3. Liquid-liquid mutual solubility data for the same binary solutions.

The data desired for the ternary systems were:

1. Isothermal vapor-liquid equilibrium data for a partially miscible ternary system.

2. Isothermal vapor-liquid equilibrium data for the constituent binary systems.

3. Mutual solubility data for the ternary system.

The desired data were not found to be available for any partially miscible binary system or for any partially miscible ternary system.

However, some information was found which was of interest to this particular research.

Based on the indirect data of total pressure measurement and liquid composition coupled with the assumption that γ_2 is unity over the mole fraction range of liquid compositions, $0 < x_1 < 0.25$, Mertes and Colburn[13] computed the constants of the two-parameter Margules equation for binary mixtures of furfural with n-butane and isobutane below the critical solution temperature. These investigators noted that linear relationships existed between the Margules constants and the reciprocal of the absolute temperature for temperatures below the critical solution temperature. Similar computations for the 1-butene-furfural binary mixture at temperatures above and below the critical solution temperature indicated such a relationship was possibly not valid both above and below the critical solution temperature. However, there was doubt concerning the accuracy of the experimental measurements and the validity of the assumptions involved in the computation of the activity coefficients from these data. Mertes and Colburn made no mention of the possibility of extrapolating the data observed below the critical solution temperature in order to obtain the values at higher temperatures above the critical solution temperature.

Based on isothermal vapor-liquid equilibrium measurements at temperatures above the critical solution temperature, Rall and Schäfer[14] found that linear relationships existed between the constants of the three-constant Redlich-Kister model and the reciprocal of the absolute temperature. Furthermore, computations based on the extrapolation of

these linear relationships allowed these investigators to calculate the binodal curve for the systems. Although the agreement between the calculated and experimental binodal curve was not excellent, it could not be considered to be entirely unsatisfactory. This work involved a great amount of graphical analysis. Furthermore, their choice of a model with three constants in lieu of four or more constants appeared to be arbitrary, since the three-constant model did not give an extremely close fit throughout the concentration range. It would seem that the use of computer techniques and higher order equations would perhaps have given even better results. Nevertheless, these investigators did produce reasonable evidence to justify an extrapolation of the linear relationship which exists above the critical solution temperature in order to investigate the region below the critical solution temperature.

Hwa[4] also observed a linear relationship between the model constants calculated from mutual solubility data and the reciprocal of the absolute temperature for temperatures below the critical solution temperature. Hwa[4] appears to have been the first investigator to suggest the use of mutual solubility data to determine the parameters of a two-constant model in order to subsequently predict the model constants at higher temperatures by means of such a linear extrapolation.

Thus, the work of Mertes and Colburn[13] suggest that the linear relationships hold in the homogeneous liquid region below the critical solution temperature. The work of Hwa[4] suggests such relationships are valid in the two-phase liquid region below the critical solution temperature. The work of Rall and Schäfer[14] indicates that linear

relationships hold above the critical solution temperature, and it further indicates that extrapolation of such relationships to lower temperatures does not give an unreasonable prediction of the mutual solubility relations. There is thus some evidence to infer that the extrapolation of the linear relationships based on mutual solubility will coincide with the linear relationship which seems to hold above the critical solution temperature.

One should bear in mind that the above inference was not firmly supported by the experimental results. For example, the observations of Mertes and Colburn (P - x data) involved an assumption concerning the value of the activity coefficient of one component. This assumption was never justified on the basis of the experimental data. Furthermore, their observations were confined to the homogeneous liquid region on only one side of the binodal curve, but a two-constant model was assumed to describe the behavior of the system on both sides of the binodal curve. The observations of Hwa assumed that a two-constant model described the behavior of the systems, but Hwa had no experimental basis to justify such an assumption. The observations of Rall and Schäfer[14] were based on a three-constant model, while the other investigators used a two-constant model. And finally, there seems to be no system which was common to the work of these investigators. Mertes and Colburn worked with hydrocarbon--furfural systems. Hwa worked with hydrocarbon--nitroethane systems, and the other investigators worked with hydrocarbon--acetone systems.

Insofar as ternary systems are concerned, no isothermal vapor-liquid data for a partially miscible ternary system were found. Severns,

et al.[15] did investigate the vapor-liquid equilibrium for three completely miscible ternary systems and the constituent binary pairs under isothermal conditions. They concluded that the ternary equilibrium could be satisfactorily predicted from the binary correlation constants if the system exhibited positive deviations from Raoult's law (i.e., $\gamma_i \geq 1.0$) throughout the concentration range. The ternary data for a system which exhibited both positive and negative deviations from Raoult's law were not adequately predicted from the binary correlation constants alone. Severns *et al.*[15] stressed that these generalizations needed further testing on other systems.

Since no ternary isothermal vapor-liquid data for a partially miscible system were found, and the desired type of binary data were not found, a decision was made to measure experimentally the necessary vapor-liquid equilibrium data for some specific systems for which the mutual solubility data had been previously reported in the literature. The systems chosen were the hydrocarbon--nitroethane systems investigated by Hwa[4] and Techo[3]. Hwa reported the binary mutual solubility data and Techo reported the ternary mutual solubility data for the systems chosen for this research. The thermodynamic behavior of hydrocarbon--nitroethane solutions has only recently been studied. It was felt that the investigation of vapor-liquid phase equilibria in these particular systems would be a significant contribution to the knowledge of these systems.

In the following chapters of this work the details of the research are presented. Chapter II describes the experimental apparatus

and materials used. Chapter III presents the description of the experimental procedure. Chapter IV is a discussion of the results of this work. Chapter V presents the conclusions. The appendices contain the bulk of the experimental data and computations.

CHAPTER II

EXPERIMENTAL APPARATUS AND MATERIALS USED

The Experimental Apparatus.--The data which are experimentally measured during the course of a vapor-liquid equilibrium experiment are as follows:

1. The composition of the vapor and the composition of the liquid samples in equilibrium.

2. The temperature of the vapor and liquid samples in equilibrium.

3. The total pressure of the vapor and liquid samples in equilibrium.

Hence, the following items of equipment are essential for the experimental measurement of vapor-liquid equilibrium data:

1. A vapor-liquid equilibrium still.

2. A manostat.

3. A manometer.

4. A temperature measuring device.

5. Analytical instruments for determining the equilibrium vapor and liquid compositions.

The specific choices of these five general types of instruments are discussed in the following sections.

Vapor-Liquid Equilibrium Still.--A comprehensive review of the various types of vapor-liquid equilibrium stills which have been used successfully

was presented by Hala et al.[16]. In general, an equilibrium still is classified according to one of five different types:

1. Distillation.
2. Circulation of vapor and circulation of liquid.
3. Static.
4. Dew and bubble point.
5. Flow type.

These five general types are discussed in detail by Hala et al.[16]. Drawings of twenty-six different stills are given, and the advantages and disadvantages of each are presented. Vilim et al.[6] point out several basic requirements that must be fulfilled in vapor-liquid equilibrium stills in order that the samples of vapor and liquid withdrawn from the still actually have the equilibrium composition and that the instrument operates economically and as simply as possible.

1. Concentration gradients must not occur in the boiling liquid.
2. The equilibrium vapor must not partially condense.
3. The walls of the boiling flask must not be superheated in order to avoid nonequilibrium total evaporation of adhering droplets of liquid.
4. The cold condensate returned to the distillation flask must be perfectly mixed with the main portion of liquid, in order to avoid its nonequilibrium vaporization as a result of its lower boiling point.
5. The vapor leaving the boiling liquid must not entrain droplets of liquid and carry them into the vapor receiver.

6. The instrument must make possible the accurate measurement of the boiling point.

7. Mixing of the equilibrium liquid with part of the returning condensate should not occur on stopping the instrument.

8. Equilibrium should be established as quickly as possible.

9. The consumption of substances should be as small as possible.

10. The instrument should be as simple as possible.

In the choice of an instrument suitable for measuring the vapor-liquid equilibrium of a given binary or multicomponent system, it is first of all necessary to consider the conditions under which the measurements will be made (temperature, pressure), further individual difficulties which can occur with certain systems (decomposition by heat, limited miscibility) and finally, the precision of the determination.

The flow-type still of Vilim *et al.*[6] was chosen for this research. Unlike most other type stills, the flow-type still can be used to measure the vapor-liquid equilibrium in systems which exhibit partial miscibility. Since the systems of interest in this research were partially miscible the use of most other type stills was excluded. Furthermore, Cantoni and Feldman[7] reported that prolonged heating of distillation residues of nitroethane at atmospheric pressure leads to violent explosions. Since the equilibrium measurement in the flow-type still is completed in a matter of minutes as compared with a matter of some hours for the other type stills, the safety standpoint also influenced the choice of the flow-type still. Insofar as the precision of the

instrument is concerned, Vilim et al.[6] demonstrated that the results which their still furnished were precise and thermodynamically consistent. The results of this research also tend to confirm this observation. A scale drawing of the flow-type equilibrium still was given by Vilim et al.[6]. The still used in this research was made of Pyrex glass, using standard taper joints, and was identical to the still described by Vilim et al. with one exception, namely, eight condensate receiver tubes were used in this research instead of four. The details of construction given by Vilim et al. were sufficient to allow the still to be constructed without further modification.

The Manostat for Pressure Control.--The manostat chosen for this research was a modification of the Williams[8] manostat. The manostat maintained a constant pressure to within ± 0.01 mm. Hg. The details of construction and a scale drawing were presented by Vilim et al.[6].

The Manometer for Pressure Measurements.--For determining the total system pressure, an absolute type U-tube mercury manometer was constructed of Pyrex glass. To minimize capillary corrections, the inside diameter of the tube was chosen to be 19 mm. The height of the mercury column was measured by comparison with a standard meter bar graduated in 0.1 cm. intervals. The 0.1 cm. subintervals of the meter bar were interpolated to 0.005 cm. by means of a cathetometer. The meter bar was located vertically within two seconds of arc. The entire manometer system was designed to meet the specifications described in NBS Monograph 8[17], such that the total error after correction to standard

gravity and 0°C. was no greater than 0.1 mm. Hg. The actual error in the pressure measurements was estimated to be ± 0.05 mm. Hg., based on vapor pressure measurements.

Appendix A presents the serial numbers and other pertinent information relating to the cathetometer and the standard meter bar. Appendix B presents the correction tables used to correct the mercury height to standard gravity and 0°C.

Temperature Measurement.--In order to have meaningful data for vapor-liquid equilibrium calculations, it is necessary to know the equilibrium temperature accurately. For the purposes of this research, a copper-constantan thermocouple was chosen to determine the equilibrium temperature. The copper wire was Anaconda 32-gauge double-glass-wrapped wire. The constantan wire was Advance 32-gauge double-glass-wrapped wire. The junctions of the thermocouple were made by carefully cleaning the ends of the copper and constantan wires with emery paper, twisting the ends together with a few turns, and then soldering the ends with rosin core solder. After the soldered joints were cool, the junctions were dipped into General Electric Insulating Varnish (Number 7031). The varnish was dried at room temperature for one hour, then the joints were re-dipped and dried three more times. The varnished wires were then put into an oven at 110°C. for one hour to bake the varnish into a hard coating.

In order to insure good heat transfer from the inside of the equilibrium chamber through the glass wall to the thermocouple, a small amount of mercury was poured into the thermocouple well which extended

into the equilibrium chamber. The varnish coating protected the junction from the mercury.

The thermocouple was calibrated in a constant temperature bath, using an NBS certified mercury thermometer (see Appendix A and Appendix B), graduated in 0.1 degree centigrade subintervals. All temperatures reported in this research are based on the International Temperature Scale. A total of fourteen data points were obtained during the calibration. The EMF of the thermocouple was measured by a Leeds and Northrup type K-3 potentiometer used in conjunction with a Leeds and Northrup type E galvanometer (see Appendix A). The data points were fitted by a smooth orthogonal polynomial of the fourth degree, and interpolated values were calculated from the polynomial fit. The polynomial gave EMF (microvolts) as a function of the temperature (°C.). The maximum deviation of the fitted curve from the data points corresponded to 0.025°C. and occurred at 80°C. Appendix A presents the serial numbers of the potentiometer and galvanometer. Appendix B presents the polynomial coefficients and the experimental calibration data points along with several calculated values for EMF versus temperature.

Analytical Instruments.--Listed below are the instruments used to determine the compositions of the liquid mixtures.

1. Bausch and Lomb Precision Sugar Refractometer.
2. Perkin-Elmer Model 154-C Vapor Fractometer.
3. Perkin-Elmer Model 154-D Vapor Fractometer, with flame ionization detector and a 300-foot x 0.01-inch Perkin-Elmer Golay type "Q" column (Apiezon "L" grease).

The normal octane-nitroethane system was analyzed for composition by using a Perkin-Elmer Model 154-C vapor Fractometer. The sample to be analyzed first passed through a two-meter Perkin-Elmer Type K column (polyethylene glycol) and then through a two-meter Perkin-Elmer Type A column (di-isodecylphthalate). The columns were made of 1/4-inch stainless steel tubing and were operated at 110°C. with a pressure drop of 25 psig across the columns. All other systems were analyzed on the Perkin-Elmer Model 154-D vapor Fractometer with the flame ionization detector and 300-foot Golay "Q" type column. The column temperature was maintained at 100°C. for the systems involving normal octane and iso-octane, and at 70°C. for the other systems. The pressure drop across the column was maintained at 30 psig for all the runs. The method of internal normalization, coupled with the bracketing method, as described by Keulemans[32] was used to determine the compositions. For the normal octane system the analyses were based on areas. Peak heights were used for all other systems.

Materials Used.--The hydrocarbons used in this research (except for benzene) were donated by the Phillips Petroleum Company. The nitroethane and nitromethane were donated by the Commercial Solvents Corporation. The benzene was Baker Reagent Grade Benzene. Those chemicals which were not at least 99 mole per cent purity as received were further purified. The physical properties measured in this research and the methods of purification are presented in Appendix C.

Equipment Layout.--Figure 1 presents a block drawing which indicates the manner in which the various items of equipment were connected.

Referring to Figure 1, the equilibrium still (A), the manometer (C), and the manostat (E) have been described. The surge vessels (D and F) each consisted of a 20-liter pyrex jar. Dry ice and methanol were used in the cold trap (B).

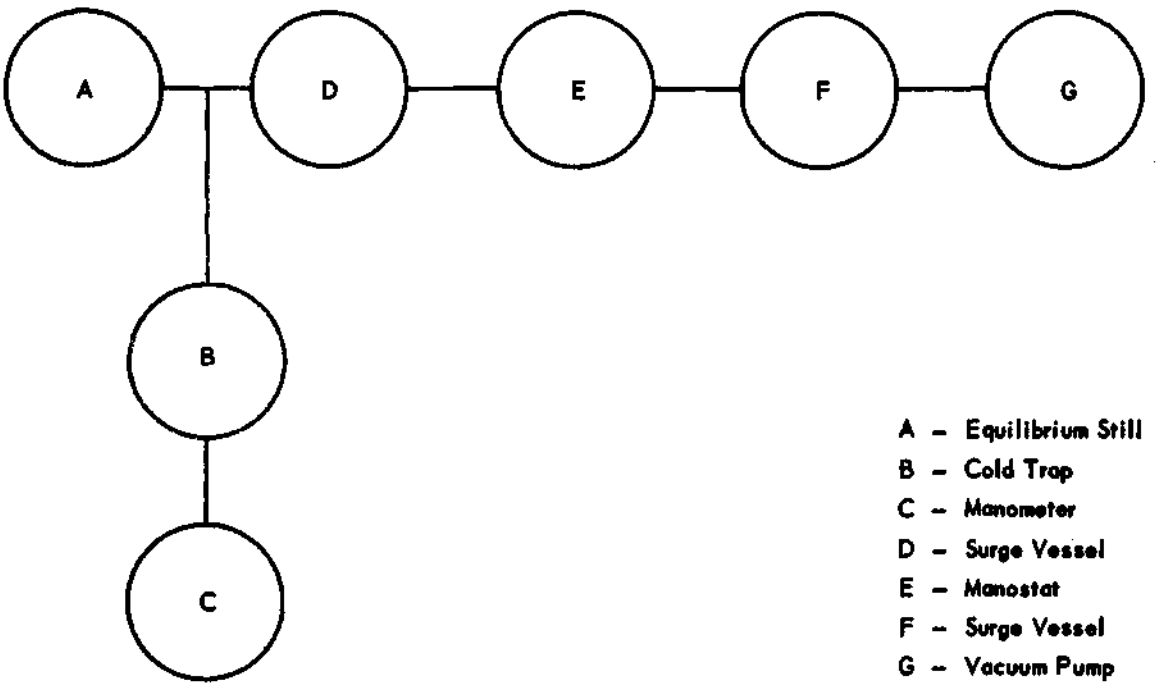

Figure 1. Diagram of Apparatus Layout.

CHAPTER III

EXPERIMENTAL PROCEDURE

An experimental run involved the following sequence of operations. The feed reservoir of the equilibrium still was filled with liquid at atmospheric pressure. The system pressure was slowly decreased until the pressure in the equilibrium chamber was slightly greater than the equilibrium pressure corresponding to the desired equilibrium temperature. Then the heaters were turned on to cause the liquid to boil. The system pressure was further decreased until the thermocouple indicated the proper temperature. The manostat was set to maintain the system pressure constant. It should be clear from this description that sometimes two or more runs were necessary for a given liquid composition in order to bracket the total pressure sufficiently closely to obtain the desired operating temperature before the liquid supply in the feed reservoir was exhausted (125 ml. reservoir capacity). After ten to fifteen milliliters of liquid were collected in a receiver tube, the condensate was diverted to another receiver tube. The top and bottom heater voltages were adjusted by trial and error such that the ratio of the amount of liquid phase collected to the amount of condensed vapor phase collected was between one and two. When the feed reservoir was almost empty, the condensate was diverted to a waste tube, the heaters were turned off, and then the manometer column height was measured to determine the system pressure.

The maximum time required for the manometer measurement was about three minutes. During this time the manostat held the system pressure constant to within 0.01 mm. Hg.

The time lapse between the initial heating and the completion of the run was usually fifteen to twenty minutes. The total run time was always limited by the capacity of the liquid feed reservoir (125 ml.).

The height of the mercury column of the manometer was corrected to 0°C. and standard gravity (i.e., "standard millimeters of mercury") by applying temperature and gravity corrections for the mercury density, the length of the standard meter bar, and local gravity (Appendix B).

A set of uncorrected experimental data for each run consisted of the following:

1. A thermocouple EMF (read to 0.1 μv).
2. Room temperature (read to 0.1°C.).
3. Total pressure (uncorrected, read to 0.005 cm. Hg.).
4. Equilibrium compositions of the vapor and liquid.

From the above set of data the final results were expressed as:

1. Equilibrium pressure (standard mm. Hg.).
2. Equilibrium temperature (°C.).
3. Equilibrium compositions of the vapor and liquid.

Based on vapor pressure measurements conducted in the equilibrium still (Appendix C), the error in the final corrected pressure was found to be less than 0.1 mm. Hg. and the error in the equilibrium temperatures was less than 0.02°C. Chromatographic analysis was generally

found to be in error by less than 0.0005 mole fraction unit for the binary mixtures and 0.003 mole fraction unit for the ternary mixture.

CHAPTER IV

DISCUSSION OF RESULTS

The Systems Investigated.--Appendix D contains summaries of the experimental data. Table 7 through Table 15 present the experimental binary vapor-liquid equilibrium data. The liquid molal volumes, and the second virial coefficients used in the computations for the systems are presented in Table 17. Table 16 tabulates the experimental ternary vapor-liquid equilibrium data.

Thermodynamic Consistency Tests.--In this section the method of testing the thermodynamic consistency of the experimental isothermal vapor-liquid data will be described. As previously mentioned, the term "vapor-liquid data" will mean a set of experimentally measured (x, y, P, T) values. First, general statements will be made describing each of the two consistency tests. This will be followed by a presentation of some of the mathematical equations involved in the consistency tests. Then a general description of each of the two methods will be presented, and finally the thermodynamic consistency of the data measured during the course of this research will be discussed in the light of the results of each of these two consistency tests. For the purpose of brevity the two consistency tests will be given specific names:

1. The Techo Consistency Test (TCT).
2. The Direct Consistency Test (DCT).

Hereafter, in this section the two methods will be referred to simply as the TCT or the DCT.

The TCT was based on the necessary and sufficient condition for the thermodynamic consistency, namely, the Gibbs-Duhem relation. Techo[3] described the TCT in detail, and the reader is referred to Reference (3) for the detailed derivation and use of the TCT. The TCT will be described only from a general viewpoint in this section.

The DCT was derived by this author during the course of this research. The DCT is based on a sufficient condition for thermodynamic consistency. The DCT involves a direct comparison of the experimentally measured (x, y, P, T) data with a calculated set of thermodynamically consistent (x, y, P, T) data. The reader is referred to Appendix H for a detailed proof and derivation of the DCT. The DCT will be described only from a general viewpoint in this section.

The mathematical starting point for this particular discussion will be Equations (2) through (6). The derivation of these equations was presented by Techo[3], and the reader is referred to Reference (3) for the details.

$$\mu_1^E = R\,T\,\ln\left(\frac{Py_1}{p_1^o x_1}\right) + (B_{11} - V_1^o)(P - p_1^o) + R_{12}\,py_2^2 \qquad (2)$$

$$\mu_2^E = R\,T\,\ln\left(\frac{Py_2}{p_2^o x_2}\right) + (B_{22} - V_2^o)(P - p_2^o) + R_{12}\,py_1^2 \qquad (3)$$

$$x_1\left(\frac{\partial \mu_1^E}{\partial x_1}\right)_T + x_2\left(\frac{\partial \mu_2^E}{\partial x_1}\right)_T - \Delta V^E\left(\frac{dp}{dx_1}\right)_T = 0 \qquad (4)$$

$$\left[\frac{RT}{P} + (B_{11} - V_1^o)x_1 + (B_{22} - V_2^o)x_2 + R_{12}(y_1^2x_1 + y_1^2x_2)\right]\frac{dP}{dy_1} \qquad (5)$$

$$+ \left[RT\left(\frac{x_1 - y_1}{y_1y_2}\right) + 2R_{12}\,P(y_1 - x_1)\right] = 0$$

$$R_{12} = 2B_{12} - B_{11} - B_{22} \qquad (5a)$$

$$G^E = x_1\mu_1^E + x_2\mu_2^E \qquad (6)$$

Equations (2) and (3) present the excess chemical potentials as functions of experimentally measurable quantities. Equation (4) is the isothermal form of the Gibbs-Duhem equation [Reference (31)]. Techo[3] obtained Equation (5) from Equations (2), (3) and (4) by assuming the term $\Delta V^E \frac{dP}{dx_1}$ in Equation (4) to be negligibly small. The TCT used Equation (5) as the constant temperature form of the Gibbs-Duhem equation, i.e., the necessary and sufficient condition for thermodynamic consistency.

In the TCT procedure the experimental quantities of total pressure, P, and vapor composition, y, were each determined as functions of liquid composition, x, using K different orthogonal polynomials of degrees 2,3, ..., K (where $K + 1 \leq N$, and N is the number of experimental data points), by means of the method of least squares. Every combination of the pairs of fitting polynomials of total pressure [$P = p(x)$] and vapor composition [$Y = y(x)$] was used to generate M equally spaced pseudo-data points. The pseudo data were spaced at liquid composition intervals of 0.01 mole fraction unit

throughout the interval $0 \leq x \leq 1$, provided the experimental data were distributed fairly uniformly throughout the concentration domain $0 \leq x \leq 1$.

However, if experimental measurements were reported in two separate intervals $0 \leq x \leq a$ and $b \leq x \leq 1$, where $a << b$ (an example is a partially miscible system for which no data were reported in the two-phase liquid-liquid region), the pseudo-data points were spaced at liquid composition intervals of 0.01 mole fraction unit on the two intervals $0 \leq x \leq a$ and $b \leq x \leq 1$. The derivatives $dP/dx = p'(x)$ and $dy/dx = y'(x)$ were also computed at these pseudo-data points. Each of these computed values, along with the values of vapor-pressure, liquid molal volumes and second virial coefficients were substituted into the left-hand side of Equation (5) to give a value, σ_i, for each of the M pseudo-data points. That pair of polynomials, $P = p(x)$ and $Y = y(x)$ for which $\sum_{i=1}^{M} (\sigma_i)^2$ was a minimum was said to characterize the experimental data in the best possible manner with regard to thermodynamic consistency. Based on the results of nineteen systems, Techo concluded that experimental vapor-liquid equilibrium data for which $\sum_{i=1}^{100} (\sigma_i)^2 < 200$ (liter-atm/mole)^2 might be considered to be thermodynamically consistent and that this furthermore indicated careful experimental work combined with true equilibrium conditions within experimental limits.

The TCT as outlined above was applied to each binary system studied in this research. The results of this examination are presented

in Table 18 (Appendix F). The data presented in Table 18 indicates thermodynamically consistent data for the following systems:

2,2,4-trimethylpentane--nitroethane 35°C.

2,2,4-trimethylpentane--nitroethane 45°C.

Normal octane--nitroethane 35°C.

Nitromethane--benzene 45°C. [Reference (5)]

Nitromethane--benzene 45°C. [this research]

The results presented in Table 18 for the other systems indicate an insufficient number of experimental data points for all the other systems. This conclusion is based on the observation that the degrees of the best fitting $P(x)$ or $y(x)$ polynomials are equal to the maximum possible degree which could be fitted to the number of available points. Lacking more experimental data for these systems, one is forced to resolve the issue of thermodynamic consistency by some other method.

One such method would involve the selection of a thermodynamically consistent model for the excess free energy function, and the evaluation of the parameters of this function by a least squares fit to Equation (6). Then, one might reasonably conclude that if the experimental (x, y, P, T) data set were back calculated from the fitted model within the experimental error, the model chosen adequately represented the data and furthermore the data would be considered thermodynamically consistent. However, if the values calculated from the chosen model differed significantly from the experimental values to which the model were fitted, one could only conclude that either the data were not thermodynamically consistent, or the chosen model would not be

applicable to the particular system, or else both. This method is the direct method (DCT) developed in this research. Appendix H presents a proof that such a method is in fact a sufficient condition for thermodynamic consistency.

It is worthwhile to point out here that the DCT has apparently been either overlooked or regarded as a not sufficient condition by previous workers. For example, Hengstebeck[19] stated: "The fact that a set of data can be correlated by an equation that is consistent with the appropriate Gibbs-Duhem equation does not prove that the data are sound or that the correlating equation is correct; it merely shows that the correlating relationship is possible thermodynamically." This statement of Hengstebeck has been shown by this author to be only part of the truth. The proof given in Appendix H of this research shows: If a set of data be fitted by an equation for G^E that is consistent with the appropriate Gibbs-Duhem equation and which satisfies the endpoints of $G^E(1) = G^E(0) = 0$, the data are thermodynamically consistent if the values of (x, y, P, T) calculated from the fitted G^E model agree with the set of experimental (x, y, P, T) data.

This concept was not found to be presented in the literature. It appears to be a novel approach to the issue of thermodynamic consistency. The DCT has an obvious advantage over other methods which have been proposed, namely, it provides a measure of the inconsistency of the data in terms of experimentally measured quantities (x, y, P, T), rather than some quantity which is not subject to direct measurement (e.g., activity coefficient, chemical potential, or the slopes

of these quantities, etc.). Hence, the proposed DCT allows one to make a judgement, for example, in the design of a distillation column; if the engineer concludes that four significant digits of accuracy in the (x, y, P, T) data are needed, this consistency test will tell whether the data are sufficiently accurate.

In using the DCT described in Appendix H, the back calculation of the (x, y, P, T) values requires a trial and error solution, and can be somewhat tedious and time consuming if the gas phase is considered to be nonideal. The use of an electronic digital computer is recommended.

The Redlich-Kister[1] model for the excess free energy, Equation (4), was chosen for the DCT computations to determine the thermodynamic consistency of all the systems studied in this research.

$$G^E = \log_e(10)\ R\ T\ [x_1\ x_2(A_1 + A_2(x_1 - x_2) + A_3(x_1 - x_2)^2 + A_4(x_1 - x_2)^3 + A_5(x_1 - x_2)^4 + \cdots)] \quad (4)$$

The derivation and the general flexibility of Equation (4) were demonstrated by Redlich and Kister[1] and Redlich, Kister, and Turnquist[2]. Appendix E contains a discussion of the Redlich-Kister equation.

The 1-, 2-, 3-, 4-, and 5-constant Redlich-Kister excess free energy models were fitted to the experimental data for each system using standard least squares techniques. The value of the excess free energy for each experimental data point was calculated by Equations (2), (3), and (6).

All computations in this research were performed on a Burroughs 220 electronic digital computer. All computations were performed in single precision floating point arithmetic (eight digits). The computations many times were based on data which involved less than eight significant figures, and hence the choice of recording final answers to eight figures is arbitrary. Some computations are reported to eight figures in this research and some are rounded to less than eight. The reader, however, should bear in mind that no inference has been made concerning the physical meaning of any computations of this research which are reported to eight significant digits.

Appendix F contains summaries of the results of the least squares fits of the Redlich-Kister models to the experimental data. Table 19 presents the values of the binary Redlich-Kister constants obtained for the 1-, 2-, 3-, 4-, and 5-constant models. Table 20 summarizes the closeness of fit of the various models. It can be seen from Table 20 that the four-constant Redlich-Kister model adequately represents the experimental data for all the systems. For the systems at 25°C., the two-constant model seems to represent the data almost as well as the four-constant model. The five-constant model showed no significant improvement over the four-constant model for any of the systems. Therefore, on the basis of the results of Table 20 one could conclude that the four-constant model adequately represents all of the binary systems studied, and furthermore that the data are thermodynamically consistent.

One might also make the selection of the appropriate Redlich-Kister model on the basis of the accuracy with which the mutual solubility curve was reproduced.

By trial and error, solutions to Equation (8) were obtained for the 2-, 3-, 4-, and 5-constant models for those systems for which the data were determined below the critical solution temperature.

$$x_1' \gamma_1' = x_1'' \gamma_1'' \qquad (8a)$$

$$x_2' \gamma_2' = x_2'' \gamma_2'' \qquad (8b)$$

In Equation (8) x_1' is the composition of the hydrocarbon-lean phase in the two-phase region and x_1'' is the composition of the hydrocarbon-rich phase in the two-phase region. The results of the calculations were compared with the experimental mutual solubility data of Hwa, and are presented in Table 21 in Appendix F. The agreement for most models is within the experimental error for the mutual solubility quoted by Hwa[4]. These results indicate that the choice of the four-constant Redlich-Kister model to represent the data would not be a bad choice.

In the further discussions and computations relating to these systems, it will be assumed that the systems are characterized by the four-constant Redlich-Kister equations presented in Table 19.

Comparison of the Experimental Vapor-Liquid Relationships with the Relationships Calculated by Mutual Solubility Data.--It is of interest to determine how closely the binary experimental vapor-liquid relationships agree with those calculated by a two-constant model

whose parameters were determined from mutual solubility data. Using the mutual solubility data of Hwa[4] it is possible, as pointed out previously, to determine the parameters for the two-constant Redlich-Kister model. The values of these constants are presented in Table 22 (Appendix F).

As Hwa indicated, Figure 2 shows that the constants below the critical solution temperature vary linearly with the reciprocal of the absolute temperature. This led Hwa to the thought that the values of the model constants might be obtained at temperatures above the critical solution temperature by a simple extrapolation of the linear relationships which are valid below the critical solution temperature. Furthermore, since mutual solubility data can usually be measured more economically than vapor-liquid data in terms of the relative time, skill and money required to conduct the experiments, the extrapolation method, if valid, would offer many obvious advantages from an engineering design viewpoint.

Table 23 (Appendix F) presents a comparison of the calculated values of vapor composition and total pressure obtained from the four-constant Redlich-Kister model fitted to the experimental vapor-liquid equilibrium data with the corresponding values calculated from the two-constant Redlich-Kister model fitted to the mutual solubility data of Hwa, and the linear extrapolation of these constants as functions of 1/T. These results indicate good agreement in the concentration region which is between 0.1 mole fraction and 0.9 mole fraction of the hydrocarbon. Outside of this region the deviation is larger. The largest

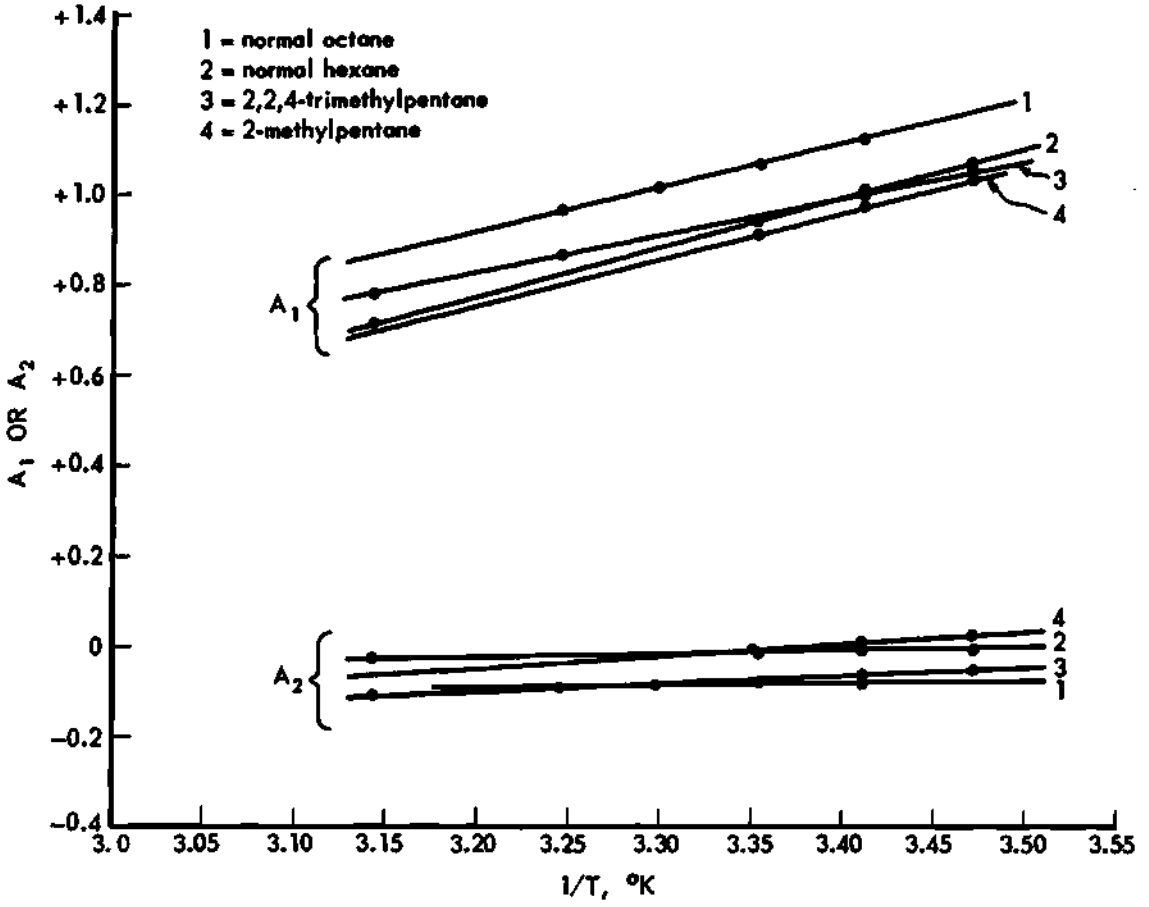

Figure 2. The Redlich-Kister Constants (Calculated from Mutual Solubility Data) Versus Reciprocal Absolute Temperature.

deviations occurred in the normal octane system at 35°C. (T_c = 41°C.) and the isooctane system at 35°C. (T_c = 30°C.), thus indicating some unusual behavior in these systems in the region near the critical solution temperature. On the other hand, the data for the normal hexane system at 25°C. (T_c = 29°C.) and the 2-methylpentane system at 25°C. (T_c = 27°C.) seem to show no unusual behavior in the region near the critical solution temperature. This anomaly was not resolved in the course of this research.

Based on the results presented in Table 23, one could conclude that for many engineering design purposes a two-constant model fitted to mutual solubility data would adequately predict the vapor-liquid relationships for these systems at temperatures which are not near the critical solution temperature. The prediction may fail to give sufficient accuracy near the critical solution temperature.

Effect of Temperature on the Constants of the Four-Constant Redlich-Kister Model.--A plot of the Redlich-Kister constants versus temperature for the 2,2,4-trimethylpentane system at 25°C., 35°C., and 45°C. (Figure 3) indicated a straight line relationship versus 1/T for the first three constants (Table 24,Appendix F). The graph of the fourth constant versus 1/T showed a curvature (concave upward) with a minimum at 35°C. The straight-line relationship of the first three constants, is, however, what one would expect on the basis of the work of Rall and Schäfer[14]. The minimum value in the plot of the fourth constant with respect to the reciprocal of the absolute temperature is probably significant in the sense that is does occur at 35°C., which is the temperature for which deviations occurred from the straight-line relationship of Hwa based on mutual

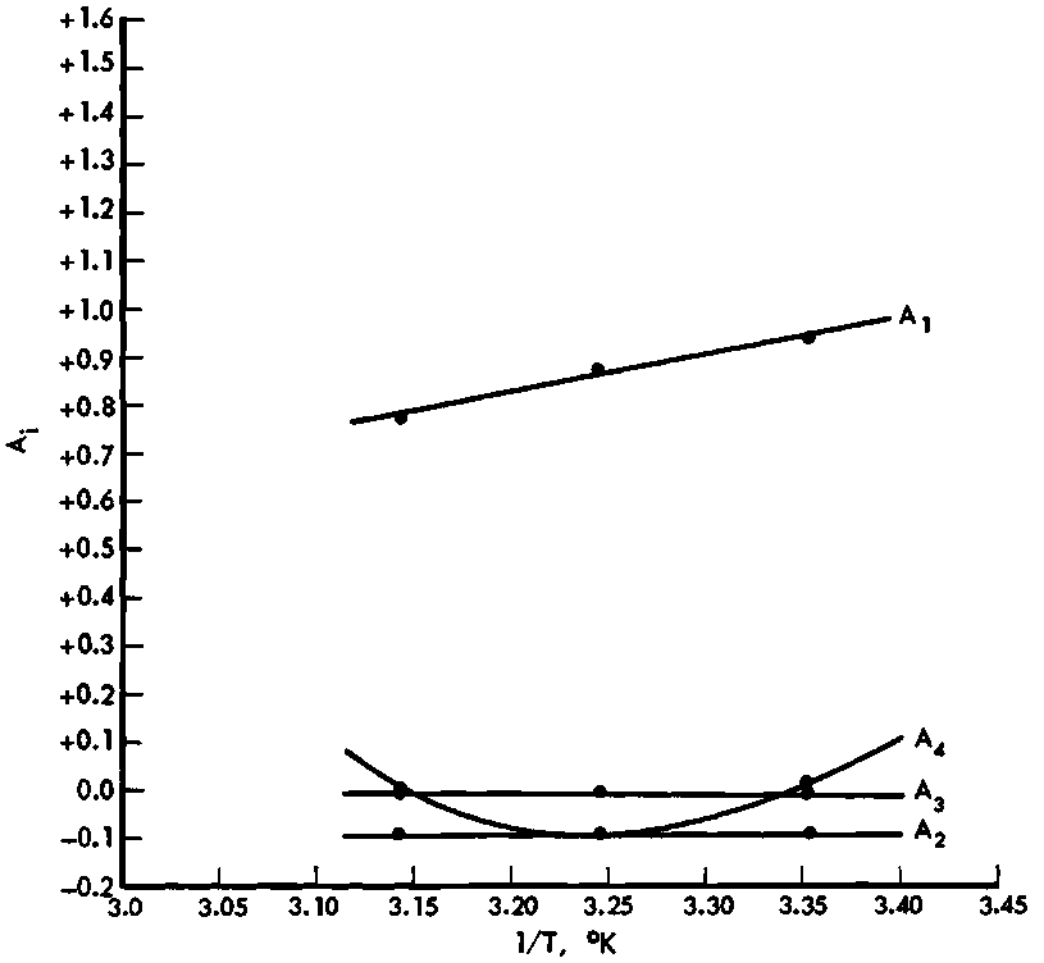

Figure 3. The Constants of the 4-Constant Redlich-Kister Excess Free Energy Model (Fitted to Vapor-Liquid Equilibrium Data) Versus Reciprocal Absolute Temperature for the 2,2,4-Trimethylpentane -- Nitroethane System.

solubility data. However, what was happening in the solution to cause this deviation was not resolved in this research.

The Characterization of the Ternary System.--The experimental vapor-liquid data were fitted by the ternary Redlich-Kister equation using 0, 1, 2, and 3 ternary interaction constants. The results show the data are best represented by using no ternary interaction constant (Table 25, Table 26). This means that this particular ternary system is adequately represented by the binary 1-2 type interaction alone. The normal octane--2,2,4-trimethylpentane pair were taken to be an ideal solution, based on the values of the binary activity coefficients calculated from two vapor-liquid equilibrium measurements made in this research.

The ternary vapor-liquid equilibrium compositions were also computed using the combination of the two-constant binary models (Table 25, Table 26). Mutual solubility data were used for the calculation of the binary constants for the normal octane--nitroethane system. For the isooctane--nitroethane pair, the previously mentioned extrapolation of the constants (based on the mutual solubility) was used to obtain the constants. The agreement with the experimental data was not entirely unsatisfactory, although it was not excellent. Certainly, in the absence of vapor-liquid equilibrium data, the use of two-constant models and mutual solubility data with the linear extrapolation process should give reasonable results. Such predictions were substantiated by the work of Techo[3].

The maximum deviation of the predictions based on mutual solubility data amounted to 0.014 mole fraction and 3.95 mm. Hg. This deviation was an order of magnitude greater than the deviation of the prediction based on the four-constant Redlich-Kister equation.

It should be kept in mind that the ternary data were compared with the experimental data only, and the experimental data covered only a limited range of the possible ternary concentration field. Thus, it is possible that the ternary prediction could be less accurate than indicated in this research. However, it is felt by this author that the work of Severns et al.[15] coupled with the work of the present research gives a firm and reasonable basis for predicting ternary vapor-liquid data from binary vapor-liquid data alone.

Summary of Calculations.--Appendix F, Table 27 presents the values of x, y, P, γ_1, γ_2, G^E, and G^M calculated at even liquid composition intervals using the four-constant Redlich-Kister model. The values in the table which are applicable to the two-phase liquid region are indicated by the following symbol, "※" .

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Several conclusions were drawn from the results of this work. These conclusions, while applying specifically to the systems studied, are presented in general form because it is believed that they may have application to other systems as well.

1. Using the Redlich-Kister two-constant model, it is possible to successfully predict the isothermal vapor-liquid phase equilibria below the critical solution temperature of a binary mixture from liquid-liquid mutual solubility data.

2. Using the Redlich-Kister two-constant model, it is possible to successfully predict the isothermal vapor-liquid equilibria of a binary mixture above the critical solution temperature by extrapolation of the mathematical model used to describe the binary mixture below the critical solution temperature. If the temperature of interest is within a few degrees of the critical solution temperature, such a prediction may be unsatisfactory.

3. Using the Redlich-Kister model, it is possible to successfully predict the isothermal vapor-liquid phase equilibria of a partially miscible ternary mixture using only a knowledge of the equilibrium properties of the constituent binary pairs.

4. A new method was developed for testing the thermodynamic consistency of vapor-liquid equilibrium data. The method uses a criterion

which was shown in this research to be a sufficient condition for thermodynamic consistency. The method has a decided advantage over the more popular slope type and area type tests in that it bases the criterion of consistency directly on the agreement with the experimentally measured set of (x, y, P, T) data.

During the course of this investigation many questions have been raised which remain unanswered. The donation of free computer time by the Rich Electronic Computer Center at Georgia Tech has made it possible to perform extensive computations which would have been otherwise impossible. Such extensive time as was used during the course of this research is not usually available on a large scale computer such as the Burroughs 220 which was used for this work. Such computations revealed the general flexibility of the Redlich-Kister excess free energy model. However, the high accuracy with which the computations were performed also indicated certain unusual characteristics of the liquid mixtures investigated in this research, such as the departure of the fourth constant of the Redlich-Kister equation from the linear $1/T$ relationship.

Two areas bear more extensive investigation by electronic digital computer methods. One is the general applicability of the straight-line relationship below the critical solution temperature for the constants of the two-constant Redlich-Kister model. This could be done by investigation of the many types of partially miscible systems for which mutual solubility data are already available.

Another area of possible future interest would be the investigation of several types of partially miscible binary systems near the

critical solution temperatures, in order to try to explain the apparent deviation from the straight-line relationship.

A third area of interest, and one also mentioned by Techo, would be to develop a method for computing the ternary constants from the ternary mutual solubility curve, in a manner similar to the binary method. All work done thus far in this area has been somewhat disappointing in its results.

And, finally, the interesting area of thermodynamic consistency testing can be further investigated by determining the limits of the applicability of the consistency test developed in this research. The test is certainly not the panacea of all problems of consistency tests. The limits of the tests and the inherent short-comings are not yet clearly delineated. Future work in this area should prove rewarding.

APPENDICES

APPENDIX A

IDENTIFICATION AND DESCRIPTION OF COMMERCIALLY MADE INSTRUMENTS USED IN THIS RESEARCH

The Standard Meter Bar.--The standard meter bar was obtained from the Gaertner Scientific Corporation, Chicago, Illinois. The Gaertner serial number was 151 AU. The bar was model number M1010. This bar was made of carpenter type 416 stainless steel, with a nominal coefficient of expansion of 9.9×10^{-6} per degree centigrade at temperatures in the near vicinity of 20°C. The bar was machine divided in millimeters and was certified to be 1,000.000 millimeters at 20°C.

The Cathetometer.--The cathetometer used in this research was obtained from the Welch Scientific Corporation. The cathetometer scale was made of stainless steel. The Georgia Tech serial number was 50246. The cathetometer scale was one meter in length, graduated in millimeters, and read to 0.05 mm. by means of a vernier. The cathetometer was only used to transfer horizontally from the mercury column to the standard meter bar, and for subsequent interpolation between millimeter divisions on the standard meter bar.

The Potentiometer.--The potentiometer was a Leeds and Northrup type K-3 model. The Leeds and Northrup serial number was 1578583.

The Galvanometer.--The galvanometer was a Leeds and Northrup type E Galvanometer. The galvanometer sensitivity was 0.5 μv/mm. deflection. The Leeds and Northrup serial number was 1578685.

Mercury Thermometer.--The mercury thermometer used for calibrating the thermocouple was a NBS certified thermometer (certificate number 143227) graduated in 0.1-degree intervals.

Refractometer.--The refractometer was a Bausch and Lomb precision sugar refractometer. The Georgia Tech serial number was 32996.

Model 154C Chromatograph.--The model 154C chromatograph was manufactured by the Perkin-Elmer Corporation. The detector was a thermistor. The Georgia Tech serial number was 63939.

Model 154D Chromatograph.--The Perkin-Elmer model 154D chromatograph was equipped with a flame ionization detector and a 300-foot x 0.01-inch Golay "Q"-type column (Apiezon "L" grease). The Georgia Tech serial number was 75503.

APPENDIX B

PRESSURE AND TEMPERATURE CONVERSION TABLES

Pressure Conversion Tables.--The pressure was corrected to standard millimeters of mercury (0°C., and standard gravity, $g_s = 980.665$ cm./sec.^{2}) by the following procedure [NBS Monograph 8[17]]. To correct for temperature, the scale error and the density error were involved:

$$h_{t_o} = F_{t_o} \cdot h_{t_1} \tag{9}$$

$$F_{t_o} = \frac{1 + s(t - t_1)}{1 + m\,t} \tag{10}$$

where F is the correction factor, $t_o = 0°C.$, t_1 is the temperature of the mercury and scale before correction, h is the height of the mercury column, s is the linear coefficient of thermal expansion of the meter scale per °C., m is the cubical coefficient of thermal expansion of mercury per °C.

For gravity correction:

$$h_g = h_{t_o} \cdot \frac{g}{g_s} \tag{11}$$

g_s = standard gravity acceleration $\equiv$ 980.665 cm./sec.^{2},

g = local gravity acceleration,

h_g = height corrected for temperature and gravity,

h_{t_o} = height corrected for temperature .

Combining Equations (9, 10, and 11) the final equation is obtained:

$$h_{corrected} = \left[\frac{1 + s(t - t_1)}{1 + m\,t}\right]\left[\frac{g}{g_s}\right] \cdot h_{t_1} \qquad (12)$$

$$h_{corrected} = F_{tg} \cdot h_{t_1}$$

For this research the following values were used:

$s = 9.9 \times 10^{-6}/°C.$,

$t_1 = 20.00°C.$,

$m = 181.8 \times 10^{-6}/°C.$ (Reference 17),

$g = 979.524$ cm./sec.^{2}; $\frac{g}{g_s} = 0.99883650.$

Substitution of these values into Equation (12) gives Equation (13):

$$F_{tg} = \frac{[1.0 + (9.9 \times 10^{-6})(T - 20.00)][0.99883650]}{(1.0 + 181.8 \times 10^{-6})} \qquad (13)$$

Various values of F_{tg} computed from Equation (13) are given in Table 2. The value of g was obtained from Reference (17).

Table 2. Pressure Correction Factors

Temperature °C.	F_{tg}
19.0	0.99538833
19.5	0.99530315
20.0	0.99521788
20.5	0.99513263
21.0	0.99504749
21.5	0.99496227
22.0	0.99487716
22.5	0.99479197
23.0	0.99470689
23.5	0.99462172
24.0	0.99453668
24.5	0.99445155
25.0	0.99436653

Thermocouple Conversion Tables.--The calibration data for the thermocouple (EMF versus temperature) were fitted by least squares, using a fourth degree orthogonal polynomial. The results of the fourth degree polynomial fit are presented in Table 3. The coefficients of the orthogonal polynomial are given in Table 4. The International Temperature Scale was used.

Table 3. Results of the Fourth Degree Polynomial Fit to the Thermocouple Calibration Data

Measured Temperature (°C.)	Measured EMF (Microvolts)	Calculated EMF (Microvolts)	Measured EMF - Calculated EMF (Microvolts)	Calculated Slope d(EMF)/dT (Microvolts/°C.)
19.95	746.25	745.93	0.32	37.94
20.00	747.75	747.82	- 0.07	37.95
21.00	785.9	785.83	0.07	38.06
21.10	789.6	789.63	- 0.03	38.07
22.60	846.75	846.86	- 0.11	38.23
25.00	938.5	938.91	- 0.41	38.48
30.00	1132.6	1132.54	0.06	38.97
36.70	1395.5	1395.68	- 0.18	39.57
40.00	1527.4	1526.72	0.68	39.85
44.975	1726.0	1725.95	0.05	40.24
59.90	2334.0	2334.77	- 0.77	41.32
80.00	3180.0	3178.95	1.05	42.68
90.00	3608.6	3609.34	- 0.74	43.41
104.10	4229.5	4229.37	0.13	44.58

Table 4. Constants for the Fourth Degree Orthogonal Polynomial, EMF = EMF(T)

i	C_i	α_i	β_i
0	0.17134535×10^{4}	----------	----------
1	0.41104151×10^{2}	0.43951785×10^{2}	0.75498571×10^{3}
2	$0.37371035 \times 10^{-1}$	0.71847905×10^{2}	0.44671227×10^{3}
3	$-0.43880609 \times 10^{-4}$	0.61362420×10^{2}	0.54607068×10^{3}
4	$0.15478878 \times 10^{-5}$	0.67608853×10^{2}	0.34717262×10^{3}

$$EMF(T) = \sum_{i=0}^{4} c_i \, t_i(T)$$

where

$$t_o(T) = 1,$$

$$t_1(T) = T \, t_o(T) - \alpha_1 \, t_o(T),$$

$$t_2(T) = (T - \alpha_2) \, t_1(T) - \beta_1 t_o(T),$$

$$t_{i+1}(T) = (T - \alpha_{i+1}) \, t_i(T) - \beta_i \, t_{i-1}(T),$$

EMF is in microvolts,

Temperature is in °C.

APPENDIX C

PHYSICAL PROPERTIES AND PURIFICATION OF MATERIALS

The Hydrocarbons.--With the exception of benzene, all hydrocarbons used in this research were donated by Phillips Petroleum Company, and were labelled by Phillips as 99-mole per cent minimum purity. Refractive index, vapor pressure measurements, and chromatographic analysis all indicated that the purity of these hydrocarbons was in fact at least 99 mole per cent. Chromatographic analyses were made on the Perkin-Elmer Model 154C chromatograph using two, two-meter Perkin-Elmer Type A (di-isodecylphthalate) columns in series.

The fractograms (plots on the recorder chart showing the variation of voltage in the detector of the Fractometer) for 2-methylpentane, 2,2,4-trimethylpentane and normal octane showed no minor peaks. The fractogram for normal hexane showed one minor peak, and the purity was estimated to be about 99.5 mole per cent based on the ratio of the areas of the minor peak and the major peak. Table 5 presents the refractive index for each hydrocarbon and Table 6 presents the measured vapor pressures at various temperatures.

Benzene.--The benzene (Baker Reagent Grade Benzene) was purified by two successive fractional crystallizations. Chromatographic analysis indicated the purified benzene was at least 99.9 mole per cent purity. The measured refractive index and the measured vapor pressures are shown in Table 5 and Table 6.

Nitromethane.--The nitromethane as received, according to the supplier, contained 99.8 weight per cent nitromethane. The major impurity was stated to be nitroethane. These results were based on a mass spectrometer analysis. However, between the time the nitromethane was received, and the time it was to be used for this research, a slight brown discoloration developed in the liquid. This discoloration was removed by two successive fractional crystallizations in a dry-ice--methanol bath. Chromatographic analysis of the recrystallized nitromethane indicated the sample was at least 99.9 mole per cent purity. The measured refractive index and the measured vapor pressures are shown in Table 5 and Table 6.

Nitroethane.--The nitroethane as received, according to a mass spectrometer analysis by the supplier, contained 0.4 per cent nitromethane, 2.9 per cent 2-nitropropane, and 96.7 per cent nitroethane. This was purified by distillation during the course of this investigation. A six-foot packed column was used for the purification, and the total absolute pressure was maintained at 100 mm. Hg. The column was operated at a reflux ratio of 30 to 1, and the middle third of each distillate batch was saved for this research. Chromatographic analysis indicated that the purified nitroethane contained at least 99.8 mole per cent nitroethane. The refractive index and the vapor pressures measured in this research are presented in Table 5 and Table 6.

Table 5. Refractive Index of Materials Used in This Research

Chemical	Grade	Refractive Index at 20.00°C. This Research	Literature Value	Reference Source	Refractive Index at 25.00°C. This Research	Literature Value	Reference Source
normal octane	Pure	1.39746	1.39743	(20)			
2,2,4-trimethyl pentane	Pure	1.39148	1.39145	(20)			
2-methyl pentane	Pure	1.37147	1.37145	(20)			
n-hexane	Pure	1.37491	1.37486	(20)			
nitromethane					1.37966	1.37964	(21)
nitroethane					1.38972	1.38973	(21)
benzene					1.49790	1.49792	(21)

Table 6. Vapor Pressures of Pure Chemicals Used in This Research

Chemical	Temperature (°C.)	Total Pressure (Std. mm. Hg.)		
		Literature Value	This Research	Reference Source
n-octane	35.00	24.08	24.08	(20)
2,2,4-trimethyl-pentane	25.00	49.34	49.35	(20)
2,2,4-trimethyl-pentane	35.00	78.23	78.22	(20)
2,2,4-trimethyl-pentane	45.00	119.80	119.79	(20)
2-methylpentane	25.00	211.76	211.75	(20)
n-hexane	25.00	151.26	151.20	(20)
n-hexane	45.00	337.71	337.82	(20)
nitromethane	45.00	93.96	93.87	(21)
nitroethane	25.00	20.92	20.93	(21)
nitroethane	35.00	35.50	35.49	(21)
nitroethane	45.00	57.84	57.85	(21)
benzene	45.00	223.51	223.60	(20)
benzene	79.15	738.01	738.30	(20)

APPENDIX D

EXPERIMENTAL VAPOR-LIQUID DATA

Table 7. Experimental Binary Vapor-Liquid Equilibrium Data

Component (1) Liquid Phase Composition Mole Fraction	Component (1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	20.92
0.0378	0.4445	36.38
0.1054	0.6248	51.40
0.1353	0.6538	54.88
0.1845	0.6793	58.19
0.7482	0.7004	58.86
0.8187	0.7336	58.20
0.9139	0.8240	55.37
0.9704	0.9236	51.91
1.0000	1.0000	49.34

Number of data points: 10

Temperature: 25.00°C.

Component (1): 2,2,4-trimethylpentane

Component (2): nitroethane

Data Source: this research

Table 8. Experimental Binary Vapor-Liquid Equilibrium Data

Component (1) Liquid Phase Composition Mole Fraction	Component (1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	35.50
0.0270	0.3920	57.01
0.0437	0.4785	65.66
0.0605	0.5287	71.90
0.0936	0.5824	79.84
0.1099	0.5978	82.36
0.1424	0.6178	85.77
0.1744	0.6299	87.86
0.1903	0.6343	88.61
0.2061	0.6379	89.23
0.2218	0.6410	89.74
0.2531	0.6461	90.54
0.3146	0.6532	91.59
0.7068	0.6763	92.62
0.7762	0.7007	92.06
0.7899	0.7081	91.81
0.8584	0.7626	89.46
0.8991	0.8125	87.02
0.9531	0.9025	82.63
0.9799	0.9567	80.12
1.0000	1.0000	78.23

Number of data points: 21

Temperature: 35.00°C.

Component (1): 2,2,4-trimethylpentane

Component (2): nitroethane

Data source: this research

Table 9. Experimental Binary Vapor-Liquid Equilibrium Data

Component (1) Liquid Phase Composition Mole Fraction	Component (1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	57.84
0.0419	0.3575	86.64
0.1178	0.5412	115.00
0.1347	0.5597	118.72
0.1931	0.6001	127.29
0.2734	0.6257	132.68
0.3452	0.6361	134.62
0.4956	0.6484	136.24
0.5765	0.6584	136.92
0.6708	0.6797	137.46
0.7918	0.7349	136.28
0.8693	0.7982	133.07
0.9718	0.9419	123.69
1.0000	1.0000	119.80

Number of data points: 14

Temperature: 45.00°C.

Component(1): 2,2,4-trimethylpentane

Component (2): nitroethane

Data source: this research

Table 10. Experimental Binary Vapor-Liquid Equilibrium Data

Component (1) Liquid Phase Composition Mole Fraction	Component (1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	35.50
0.0383	0.2007	42.90
0.0662	0.2753	46.34
0.0937	0.3214	48.63
0.1210	0.3510	50.13
0.1478	0.3702	51.09
0.7612	0.4044	50.60
0.8033	0.4251	49.03
0.8241	0.4392	47.96
0.8859	0.5058	43.26
0.9665	0.7359	31.70
0.9864	0.8664	27.43
1.0000	1.0000	24.08

Number of data points: 13

Temperature: 35.00°C.

Component (1): normal octane

Component (2): nitroethane

Data source: this research

Table 11. Experimental Binary Vapor-Liquid Equilibrium Data

Component(1) Liquid Phase Composition Mole Fraction	Component(1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	20.92
0.0455	0.7661	85.76
0.0498	0.7794	90.62
0.1056	0.8622	139.12
0.1773	0.8938	173.31
0.2143	0.9009	183.06
0.2582	0.9059	190.20
0.2618	0.9062	190.63
0.6703	0.9094	195.05
0.7945	0.9197	199.41
0.8693	0.9356	203.74
0.9601	0.9732	209.59
1.0000	1.0000	211.76

Number of data points: 13

Temperature: 25.00°C.

Component(1): 2-methylpentane

Component(2): nitroethane

Data source: this research

Table 12. Experimental Binary Vapor-Liquid Equilibrium Data

Component(1) Liquid Phase Composition Mole Fraction	Component(1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	20.92
0.0429	0.7068	68.58
0.0502	0.7329	74.82
0.1108	0.8315	113.51
0.1212	0.8390	118.06
0.1511	0.8547	128.67
0.2059	0.8703	140.86
0.2369	0.8750	144.81
0.7710	0.8823	147.62
0.8436	0.8984	149.52
0.9231	0.9337	151.40
0.9512	0.9531	151.70
1.0000	1.0000	151.26

Number of data points: 13

Temperature: 25.00°C.

Component(1): normal hexane

Component(2): nitroethane

Data source: this research

Table 13. Experimental Binary Vapor-Liquid Equilibrium Data

Component(1) Liquid Phase Composition Mole Fraction	Component(1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	57.84
0.0575	0.6156	142.64
0.1293	0.7515	208.73
0.1573	0.7748	226.12
0.2271	0.8085	255.84
0.3963	0.8389	285.79
0.4577	0.8445	290.86
0.6031	0.8587	301.33
0.6224	0.8611	302.84
0.7473	0.8833	313.94
0.8106	0.9007	320.30
0.8595	0.9182	325.33
0.9134	0.9430	330.69
0.9811	0.9852	336.45
1.0000	1.0000	337.71

Number of data points: 15
Temperature: 45.00°C.
Component(1): normal hexane
Component(2): nitroethane
Data source: this research

Table 14. Experimental Binary Vapor-Liquid Equilibrium Data

Component(1) Liquid Phase Composition Mole Fraction	Component(1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	223.51
0.0810	0.0901	227.60
0.1011	0.1060	227.90
0.1541	0.1425	227.70
0.1861	0.1624	227.10
0.2225	0.1834	226.20
0.4127	0.2689	217.10
0.5338	0.3194	208.10
0.6779	0.3834	192.90
0.7119	0.4023	188.20
0.8610	0.5378	156.90
0.9418	0.7075	126.40
0.9623	0.7785	116.30
0.9910	0.9323	99.50
1.0000	1.0000	93.96

Number of data points: 15
Temperature: 45.00°C.
Component(1): nitromethane
Component(2): benzene
Data source: this research

Table 15. Experimental Binary Vapor-Liquid Equilibrium Data

Component(1) Liquid Phase Composition Mole Fraction	Component(1) Vapor Phase Composition Mole Fraction	Total Pressure Standard mm. Mercury
0.0000	0.0000	223.74
0.0445	0.0548	226.43
0.0966	0.1026	227.83
0.1979	0.1694	226.92
0.2927	0.2173	223.50
0.3921	0.2602	218.27
0.4737	0.2942	213.14
0.5259	0.3166	208.62
0.6180	0.3543	200.11
0.7118	0.4023	188.14
0.8102	0.4765	170.13
0.9051	0.6144	142.18
0.9601	0.7708	117.19
1.0000	1.0000	93.72

Number of data points: 14
Temperature: 45°C.
Component(1): nitromethane
Component(2): benzene
Data source: Reference (5)

Table 16. Experimental Ternary Vapor-Liquid Equilibrium Data

Liquid Phase Composition* Mole Fraction	Vapor Phase Composition* Mole Fraction	Total Pressure Standard mm. Mercury
0.191	0.068	67.87
0.809	0.932	67.87
0.000	0.000	67.87
0.179	0.059	75.62
0.758	0.777	75.62
0.063	0.164	75.62
0.174	0.056	77.88
0.738	0.743	77.88
0.088	0.201	77.88
0.167	0.052	80.49
0.707	0.705	80.49
0.126	0.243	80.49
0.153	0.049	83.38
0.648	0.655	83.38
0.199	0.297	83.38
0.136	0.046	85.13
0.575	0.620	85.13
0.289	0.334	85.13
0.124	0.047	85.47
0.526	0.603	85.47
0.350	0.350	85.47
0.083	0.050	85.69
0.353	0.588	85.69
0.564	0.362	85.69
0.072	0.050	85.85
0.307	0.589	85.85
0.621	0.361	85.85

continued next page

*The tabular arrangement implies: $x_1 = 0.191$, $x_2 = 0.809$, $x_3 = 0.000$, etc. A similar arrangement is used for the vapor compositions.

Table 16 - (continued)

Liquid Phase Composition* Mole Fraction	Vapor Phase Composition* Mole Fraction	Total Pressure Standard mm. Mercury
0.060	0.052	86.01
0.256	0.587	86.01
0.684	0.361	86.01
0.047	0.050	84.91
0.200	0.577	84.91
0.753	0.373	84.91
0.033	0.050	79.80
0.138	0.543	79.80
0.829	0.407	79.80
0.017	0.044	64.81
0.070	0.432	64.81
0.913	0.524	64.81
0.008	0.032	50.63
0.032	0.281	50.63
0.960	0.687	50.63
0.000	0.000	35.50
0.000	0.000	35.50
1.000	1.000	35.50
0.529	0.257	49.58
0.471	0.743	49.58
0.000	0.000	49.58
0.511	0.219	55.96
0.455	0.635	55.96
0.034	0.146	55.96
0.494	0.198	60.51
0.441	0.572	60.51
0.065	0.230	60.51
0.475	0.180	64.43
0.423	0.522	64.43
0.102	0.298	64.43

continued next page

Table 16 - (continued)

Liquid Phase Composition^{x} Mole Fraction	Vapor Phase Composition^{x} Mole Fraction	Total Pressure Standard mm. Mercury
0.409	0.154	71.02
0.365	0.439	71.02
0.226	0.406	71.02
0.368	0.148	72.19
0.328	0.420	72.19
0.304	0.432	72.19
0.357	0.148	72.17
0.318	0.414	72.17
0.325	0.438	72.17
0.115	0.157	69.77
0.103	0.382	69.77
0.782	0.461	69.77
0.084	0.153	65.94
0.075	0.352	65.94
0.841	0.496	65.94
0.050	0.133	58.14
0.045	0.288	58.14
0.905	0.579	58.14
0.014	0.063	43.08
0.012	0.125	43.08
0.974	0.812	43.08

Temperature: 35.00°C.
Component(1): normal octane
Component(2): 2,2,4-trimethylpentane
Component(3): nitroethane
Data source: this research

APPENDIX E

THE REDLICH-KISTER EQUATION

The following discussion is not new, in that much of it can be found in the papers presented by Redlich and Kister[1] and Redlich, Kister and Turnquist[2].

The question of representing activity coefficients has been repeatedly discussed in recent years [References (26), (27), (28), (29)]. A fairly extensive experience [Reference (2)] has confirmed the belief that the following method comes closest to satisfying the requirements of flexibility and convenience.

The starting point for this discussion of activity coefficients is the function Q, which for a binary solution is defined by:

$$Q = x_1 \log_{10}(\gamma_1) + x_2 \log_{10}(\gamma_2) \qquad (14)$$

x_1 and x_2 denote the mole fractions, and γ_1 and γ_2 the activity coefficients. The development of functions like Q, log γ, etc., into power series with respect to x has been suggested already by Margules[30]. The usefulness however greatly depends on the form of the series. Wohl[28], in reviewing the various methods of representing activity coefficients, pointed out that the series should be developed in such a way that the higher terms are corrections of the terms of lower order. Also important is the fact that the coefficients of a properly chosen series furnish a natural classification of various

systems (a property of the Redlich-Kister model which we will demonstrate later).

Since $Q = 0$ for $x = 0$ and 1, each term should contain the factor $x(1 - x)$. It is desirable to develop the series with respect to a variable which is somehow symmetric with respect to the two components. Thus, the equation which Redlich and Kister developed for a binary mixture was:

$$Q_{12} = x_1(1 - x_1)[B + C(2x_1 - 1) + D(2x_1 - 1)^2 + \cdots] \qquad (15)$$

The Gibbs molal excess free energy is related to Q_{12} by:

$$G^E = \log_e(10)\ (R)\ (T)\ (Q_{12}) \qquad (16)$$

The excess chemical potential is obtained by differentiation:

$$\mu_i^E = \left(\frac{\partial[(\sum_i n_i)(G^E)]}{\partial n_i}\right)_{T,P,n_j} = RT \ln(\gamma_i) \qquad (17)$$

Thus, from (15), (16), and (17):

$$\log_{10}(\gamma_1) = x_2^2[B + C(3x_1 - x_2) + D(5x_1 - x_2)(x_1 - x_2) \qquad (18)$$
$$+ E(7x_1 - x_2)(x_1 - x_2)^2 + F(9x_1 - x_2)(x_1 - x_2)^3 + \cdots]$$

and

$$\log_{10}(\gamma_2) = x_1^2[B + C(x_1 - 3x_2) + D(x_1 - x_2)(x_1 - 5x_2) \qquad (19)$$
$$+ E(x_1 - x_2)^2(x_1 - 7x_2) + F(x_1 - x_2)^3(x_1 - 9x_2) + \cdots]$$

The method is easily extendable to ternary mixtures by:

$$Q_{123} = Q_{12} + Q_{23} + Q_{13} + M \tag{20}$$

where

$$Q_{ij} = x_i\, x_j \sum_{i=1}^{K} A_i (x_i - x_j)^{i-1} \tag{21}$$

and M is a ternary interaction constant which can be evaluated only from measurements made on the ternary system. Redlich and Kister take the functional relationship for M to be:

$$M = x_1\, x_2\, x_3 [C + D_1(x_2 - x_3) + D_2(x_3 - x_1) + \cdots] \tag{22}$$

By application of Equation (17) to Equation (21) one obtains expressions for $\log_{10}(\gamma)$.

The constants of the Redlich-Kister equation may be evaluated by the method of least squares, or by the tables presented by Redlich and Kister[1].

Referring to Equation (21), we will now discuss the classifications of the various solution types made by Relich and Kister[1].

Types of Solutions:

Type 1. $A_1 = A_2 = \cdots = 0$

Type 2. $A_1 \neq 0$, $A_2 = A_3 = \cdots = 0$

Type 3. $A_1 \neq 0$, $A_2 \neq 0$, $A_3 = A_4 = \cdots = 0$

Type 4. $A_1 \neq 0$, $A_2 = 0$, $A_3 \neq 0$, $A_4 = A_5 = \cdots = 0$

Type 5. $A_1 \neq 0$, $A_2 \neq 0$, $A_3 \neq 0$, $A_4 = A_5 = \cdots = 0$

Redlich and Kister[1] showed that Type 2 very well approximates systems, the components of which are not associated, interact only moderately, and have approximately equal molal volumes. For systems which are not associated, and interact only moderately, but which have unequal molal volumes, Type 3 was found to be adequate for the representation of the behavior of the system. Types 4 and 5 represent solutions in which association and interaction are present.

The physical interpretation of higher order nonzero constants is not clear.

APPENDIX F

SUMMARY OF THE RESULTS OF THE THERMODYNAMIC CONSISTENCY TESTS AND THE REDLICH-KISTER LEAST-SQUARES FIT TO EXPERIMENTAL VAPOR-LIQUID DATA

Table 18. Summary of the Results of the Thermodynamic Consistency Test Using the Method of Techo

System	Temperature °C.	Number of Experimental Data Points	Number of Pseudo Points Used in Test	Minimum Sums of Squares of Gibbs-Duhem Equation	Degree of Best Fitting Polynomial	
					P(x) Degree	y(x) Degree
nitromethane--benzene [Reference (5)]	45.00	14	100	65.2	6	12
nitromethane--benzene (this research)	45.00	15	100	66.2	8	12
normal hexane--nitroethane	45.00	15	100	500	14	14
normal hexane--nitroethane	25.00	13	47	>50,000	all degrees	all degrees
2-methylpentane--nitroethane	25.00	13	60	>50,000	all degrees	all degrees
2,2,4-trimethylpentane--nitroethane	25.00	10	45	2,506	5	9
2,2,4-trimethylpentane--nitroethane	35.00	21	51	29.5	11	16
2,2,4-trimethylpentane--nitroethane	45.00	14	100	59.0	8	12
normal octane--nitroethane	35.00	13	41	29.1	12	11

Table 19. Values of the Redlich-Kister Constants Determined by a Least-Squares Fit to the Experimental Vapor-Liquid Data

2,2,4-Trimethylpentane(1)--Nitroethane(2) System; 25.00°C.

Redlich-Kister 5-constant equation:

$A1 = 0.93260105$

$A2 = -0.88865136 \times 10^{-1}$

$A3 = 0.58232480 \times 10^{-3}$

$A4 = 0.51198863 \times 10^{-2}$

$A5 = -0.70212321 \times 10^{-2}$

Redlich-Kister 4-constant equation:

$A1 = 0.93416947$

$A2 = -0.89352457 \times 10^{-1}$

$A3 = -0.64126839 \times 10^{-2}$

$A4 = 0.58412618 \times 10^{-2}$

Redlich-Kister 3-constant equation:

$A1 = 0.93325255$

$A2 = -0.86456571 \times 10^{-1}$

$A3 = -0.47790144 \times 10^{-2}$

Redlich-Kister 2-constant equation:

$A1 = 0.93126896$

$A2 = -0.86009744 \times 10^{-1}$

Redlich-Kister 1-constant equation:

$A1 = 0.92735442$

continued next page

Table 19 - (continued)

2,2,4-Trimethylpentane(1)--Nitroethane(2) System; 35.00°C.

Redlich-Kister 5-constant equation:

A1 = 0.87565664
A2 = -0.10390878
A3 = 0.35194030 x 10^{-1}
A4 = -0.11260296
A5 = -0.20964637 x 10^{-1}

Redlich-Kister 4-constant equation:

A1 = 0.87845526
A2 = -0.10415183
A3 = 0.18216150 x 10^{-1}
A4 = -0.11210217

Redlich-Kister 3-constant equation:

A1 = 0.87217679
A2 = -0.14915976
A3 = 0.36824689 x 10^{-1}

Redlich-Kister 2-constant equation:

A1 = 0.88419142
A2 = -0.15036972

Redlich-Kister 1-constant equation:

A1 = 0.90793362

continued next page

Table 19 - (continued)

2,2,4-Trimethylpentane(1)--Nitroethane(2) System; 45.00°C.

Redlich-Kister 5-constant equation:

$A1 = 0.76961032$

$A2 = -0.96693002 \times 10^{-1}$

$A3 = -0.57368730 \times 10^{-2}$

$A4 = -0.31603507 \times 10^{-2}$

$A5 = -0.75268575 \times 10^{-2}$

Redlich-Kister 4-constant equation:

$A1 = 0.76986202$

$A2 = -0.97021517 \times 10^{-1}$

$A3 = -0.99343948 \times 10^{-2}$

$A4 = -0.23022472 \times 10^{-2}$

Redlich-Kister 3-constant equation:

$A1 = 0.76985941$

$A2 = -0.97855567 \times 10^{-1}$

$A3 = -0.98199304 \times 10^{-2}$

Redlich-Kister 2-constant equation:

$A1 = 0.76820248$

$A2 = -0.96904972 \times 10^{-1}$

Redlich-Kister 1-constant equation:

$A1 = 0.77285635$

continued next page

Table 19 - (continued)

Normal Octane(1)--Nitroethane(2) System; 35.00°C.

Redlich-Kister 5-constant equation:

$A1 = 0.95729508$

$A2 = -0.87917911 \times 10^{-1}$

$A3 = 0.19940990 \times 10^{-1}$

$A4 = 0.25558778 \times 10^{-2}$

$A5 = -0.31423312 \times 10^{-2}$

Redlich-Kister 4-constant equation:

$A1 = 0.95812621$

$A2 = -0.88233053 \times 10^{-1}$

$A3 = 0.16621525 \times 10^{-1}$

$A4 = 0.30811227 \times 10^{-2}$

Redlich-Kister 3-constant equation:

$A1 = 0.95746603$

$A2 = -0.86502433 \times 10^{-1}$

$A3 = 0.17572000 \times 10^{-1}$

Redlich-Kister 2-constant equation:

$A1 = 0.96567647$

$A2 = -0.88895492 \times 10^{-1}$

Redlich-Kister 1-constant equation:

$A1 = 0.94866246$

continued next page

Table 19 - (continued)

2-Methylpentane(1)--Nitroethane(2) System; 25.00°C.

Redlich-Kister 5-constant equation:

$A1 = 0.89561665$

$A2 = 0.33766775 \times 10^{-2}$

$A3 = -0.96676788 \times 10^{-2}$

$A4 = 0.12488130 \times 10^{-1}$

$A5 = -0.97900644 \times 10^{-2}$

Redlich-Kister 4-constant equation:

$A1 = 0.89676399$

$A2 = 0.25830113 \times 10^{-2}$

$A3 = -0.17313397 \times 10^{-1}$

$A4 = 0.14224601 \times 10^{-1}$

Redlich-Kister 3-constant equation:

$A1 = 0.89695718$

$A2 = 0.79493430 \times 10^{-2}$

$A3 = -0.18058943 \times 10^{-1}$

Redlich-Kister 2-constant equation:

$A1 = 0.89172390$

$A2 = 0.88449573 \times 10^{-2}$

Redlich-Kister 1-constant equation:

$A1 = 0.89043525$

continued next page

Table 19 - (continued)

Normal Hexane(1)--Nitroethane(2) System; 25.00°C.

Redlich-Kister 5-constant equation:

$A1 = 0.93198489$

$A2 = -0.44912841 \times 10^{-2}$

$A3 = 0.50626191 \times 10^{-2}$

$A4 = 0.87299339 \times 10^{-2}$

$A5 = -0.20037240 \times 10^{-1}$

Redlich-Kister 4-constant equation:

$A1 = 0.93625612$

$A2 = -0.44295301 \times 10^{-2}$

$A3 = -0.14653470 \times 10^{-1}$

$A4 = 0.84317715 \times 10^{-2}$

Redlich-Kister 3-constant equation:

$A1 = 0.93680416$

$A2 = -0.50510091 \times 10^{-3}$

$A3 = -0.15911008 \times 10^{-1}$

Redlich-Kister 2-constant equation:

$A1 = 0.93028287$

$A2 = -0.23908513 \times 10^{-3}$

Redlich-Kister 1-constant equation:

$A1 = 0.93032722$

continued next page

Table 19 - (continued)

Normal Hexane(1)--Nitroethane(2) System; 45.00 °C.

Redlich-Kister 5-constant equation:

$A1 = 0.70562210$

$A2 = -0.26681127 \times 10^{-1}$

$A3 = -0.12868491 \times 10^{-1}$

$A4 = 0.17392501 \times 10^{-1}$

$A5 = -0.82799773 \times 10^{-2}$

Redlich-Kister 4-constant equation:

$A1 = 0.70586437$

$A2 = -0.26456258 \times 10^{-1}$

$A3 = -0.17525661 \times 10^{-1}$

$A4 = 0.16988579 \times 10^{-1}$

Redlich-Kister 3-constant equation:

$A1 = 0.70566867$

$A2 = -0.19800528 \times 10^{-1}$

$A3 = -0.17443597 \times 10^{-1}$

Redlich-Kister 2-constant equation:

$A1 = 0.70263068$

$A2 = -0.19639251 \times 10^{-1}$

Redlich-Kister 1-constant equation:

$A1 = 0.70181190$

Table 20. Closeness of Fit of the Redlich-Kister Model to the Experimental Vapor-Liquid Equilibrium Data

Type RK Equation	System Name	Maximum Absolute Deviation $y_{calc} - y_{exp}$	Maximum Absolute Deviation $P_{calc} - P_{exp}$	System Temperature °C.
1	A※	0.0416	2.81	25.00
2	A※	0.0005	0.06	25.00
3	A※	0.0005	0.01	25.00
4	A※	0.0005	0.02	25.00
5	A※	0.0005	0.02	25.00
1	A※	0.0821	7.88	35.00
2	A※	0.0203	3.66	35.00
3	A※	0.0647	2.17	35.00
4	A※	0.0005	0.04	35.00
5	A※	0.00007	0.05	35.00
1	A※	0.0378	5.54	45.00
2	A※	0.0009	0.17	45.00
3	A※	0.0010	0.19	45.00
4	A※	0.0003	0.03	45.00
5	A※	0.0002	0.03	45.00
1	B※	0.0303	2.08	35.00
2	B※	0.0706	0.60	35.00
3	B※	0.0014	0.08	35.00
4	B※	0.0005	0.04	35.00
5	B※	0.0008	0.04	35.00
1	C※	0.0378	0.89	25.00
2	C※	0.0004	0.15	25.00
3	C※	0.0005	0.13	25.00
4	C※	0.0005	0.15	25.00
5	C※	0.0005	0.15	25.00

continued next page

※ system identification

A = 2,2,4-trimethylpentane--nitroethane

B = normal octane--nitroethane

C = normal hexane--nitroethane

D = 2-methylpentane--nitroethane

Table 20 - (continued)

Type RK Equation	System Name	Maximum Absolute Deviation $y_{calc} - y_{exp}$	Maximum Absolute Deviation $P_{calc} - P_{exp}$	System Temperature °C.
1	C⊗	0.0122	5.55	45.00
2	C⊗	0.0012	0.82	45.00
3	C⊗	0.0008	0.68	45.00
4	C⊗	0.0001	0.04	45.00
5	C⊗	0.0001	0.06	45.00
1	D⊗	0.0025	0.96	25.00
2	D⊗	0.0002	0.16	25.00
3	D⊗	0.0002	0.16	25.00
4	D⊗	0.0002	0.16	25.00
5	D⊗	0.0002	0.09	25.00

Table 21. Comparison of Experimental Mutual Solubility Data with Values Predicted by the Redlich-Kister Fit to Experimental Vapor-Liquid Data

Type RK Equation (No. of Const.)	System	Temp. °C.	Calc. x_1'	Calc. x_1''	Exp. x_1' (Hwa)	Exp. x_1'' (Hwa)	x_1' Difference Calc.- Exp.	x_1'' Difference Calc.- Exp.
2	A※	25.00	0.204	0.689	0.206	0.688	- 0.002	0.001
3	A※	25.00	0.206	0.686	0.206	0.688	0.000	- 0.002
4	A※	25.00	0.206	0.689	0.206	0.688	0.000	0.001
5	A※	25.00	0.205	0.687	0.206	0.688	- 0.001	- 0.001
2	B※	35.00	> 0.192	< 0.694	0.187	0.700	> 0.005	< - 0.006
3	B※	35.00	0.192	0.695	0.187	0.700	0.005	- 0.005
4	B※	35.00	0.189	0.699	0.187	0.700	0.002	- 0.001
5	B※	35.00	0.186	0.704	0.187	0.700	- 0.001	0.004
2	C※	25.00	0.257	0.726	0.259	0.725	- 0.002	0.001
3	C※	25.00	0.258	0.725	0.259	0.725	- 0.001	0.000
4	C※	25.00	0.259	0.726	0.259	0.725	0.000	0.001
5	C※	25.00	0.259	0.725	0.259	0.725	0.000	0.000
2	D※	25.00	0.317	0.667	0.319	0.665	- 0.002	0.002
3	D※	25.00	0.319	0.665	0.319	0.665	0.000	0.000
4	D※	25.00	0.319	0.665	0.319	0.665	0.000	0.000
5	D※	25.00	0.316	0.667	0.319	0.665	- 0.003	0.002

※ system identification

A = 2,2,4-trimethylpentane--nitroethane

B = normal octane--nitroethane

C = normal hexane--nitroethane

D = 2-methylpentane--nitroethane

Table 22. The Redlich-Kister Constants Calculated from Hwa's Mutual Solubility Data

A_1	A_2	Temperature °C.	System
1.1183	- 0.0912	20	normal octane--nitroethane
1.0625	- 0.0955	25	normal octane--nitroethane
1.0064	- 0.0978	30	normal octane--nitroethane
0.9472	- 0.0989	35	normal octane--nitroethane
1.0504	- 0.0556	15	2,2,4-trimethylpentane--nitroethane
0.9971	- 0.0719	20	2,2,4-trimethylpentane--nitroethane
0.9361	- 0.0877	25	2,2,4-trimethylpentane--nitroethane
0.865 ※	- 0.095 ※	35	2,2,4-trimethylpentane--nitroethane
0.775 ※	- 0.105 ※	45	2,2,4-trimethylpentane--nitroethane
1.0661	- 0.0041	15	normal hexane--nitroethane
1.0064	- 0.0097	20	normal hexane--nitroethane
0.9413	- 0.0124	25	normal hexane--nitroethane
0.710 ※	- 0.030 ※	45	normal hexane--nitroethane
1.0312	+ 0.0214	15	2-methylpentane--nitroethane
0.9718	+ 0.0046	20	2-methylpentane--nitroethane
0.9057	- 0.0106	25	2-methylpentane--nitroethane

※ Values of A_1 and A_2 obtained by extrapolation of the values at lower temperatures (plot of A_1 versus $1/T$ and plot of A_2 versus $1/T$).

Table 23. Comparison of the 4-Constant Redlich-Kister Equation Fitted by Least Squares to the Experimental Vapor-Liquid Data with the 2-Constant Redlich-Kister Equation Fitted to Experimental Solubility Data

System	Temp. °C.	x Mole Fract.	4-Const. y Mole Fract.	4-Const. P mm. Hg.	2-Const. y Mole Fract.	2-Const. P mm. Hg.	$y_4 - y_2$ Mole Fract.	$P_4 - P_2$ mm. Hg.	Max. y Diff. Mole Fract.	Max. P Diff. mm. Hg.
A⊗	35.00	0.01	0.0701	37.81	0.0671	37.68	0.0030	0.13		
A⊗	35.00	0.10	0.3290	49.01	0.3240	48.59	0.0050	0.42		
A⊗	35.00	0.18	0.3841	51.74	0.3816	51.38	0.0025	0.36		
A⊗	35.00	0.70	0.3873	51.83	0.3840	51.47	0.0033	0.36		
A⊗	35.00	0.80	0.4232	49.15	0.4252	48.45	-0.0020	0.70		
A⊗	35.00	0.90	0.5291	41.77	0.5422	40.62	0.0131	1.15	0.0131	1.15
A⊗	35.00	0.99	0.8968	26.59	0.9075	26.28	0.0107	0.31		
B⊗	25.00	0.01	0.4476	37.50	0.4466	37.45	0.0010	0.05	0.0010	
B⊗	25.00	0.10	0.8580	135.46	0.8577	135.27	0.0003	0.19		0.19
B⊗	25.00	0.20	0.8985	179.74	0.8984	179.62	0.0001	0.12		
B⊗	25.00	0.30	0.9085	193.91	0.9084	193.82	0.0001	0.09		
B⊗	25.00	0.67	0.9094	195.03	0.9093	194.93	0.0001	0.10		
B⊗	25.00	0.70	0.9107	195.71	0.9106	195.62	0.0001	0.09		
B⊗	25.00	0.80	0.9206	199.67	0.9206	199.60	0.0000	0.07		
B⊗	25.00	0.90	0.9455	205.71	0.9455	205.67	0.0000	0.04		
B⊗	25.00	0.99	0.9925	211.27	0.9925	211.26	0.0000	0.01		
C⊗	25.00	0.01	0.3870	33.79	0.3854	33.72	0.0016	0.07	0.0016	
C⊗	25.00	0.10	0.8220	108.20	0.8216	108.00	0.0004	0.20		0.20
C⊗	25.00	0.20	0.8692	139.91	0.8691	139.84	0.0001	0.07		
C⊗	25.00	0.25	0.8765	146.04	0.8765	146.01	0.0000	0.03		
C⊗	25.00	0.73	0.8776	146.76	0.8776	146.76	0.0000	0.00		
C⊗	25.00	0.80	0.8873	148.32	0.8874	148.33	-0.0001	- 0.01		
C⊗	25.00	0.90	0.9208	150.95	0.9209	150.96	-0.0001	- 0.01		
C⊗	25.00	0.99	0.9888	151.48	0.9887	151.48	0.0001	0.00		

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Table 23 - (continued)

System	Temp. °C.	x Mole Fract.	4-Const. y Mole Fract.	4-Const. P mm. Hg.	2-Const. y Mole Fract.	2-Const. P mm. Hg.	$y_4 - y_2$ Mole Fract.	$P_4 - P_2$ mm. Hg.	Max. y Diff. Mole Fract.	Max. P Diff. mm.Hg.
C⊗	45.00	0.01	0.2382	75.18	0.2380	75.16	0.0002	0.02		
C⊗	45.00	0.10	0.7151	185.96	0.7123	184.30	0.0028	1.66	0.0028	
C⊗	45.00	0.20	0.7982	246.20	0.7961	243.71	0.0021	2.49		2.49
C⊗	45.00	0.30	0.8262	273.37	0.8254	271.63	0.0008	1.74		
C⊗	45.00	0.40	0.8392	286.12	0.8396	285.51	-0.0004	0.61		
C⊗	45.00	0.50	0.8482	293.88	0.8494	294.03	-0.0012	-0.15		
C⊗	45.00	0.60	0.8583	301.08	0.8597	301.47	-0.0014	-0.39		
C⊗	45.00	0.70	0.8734	309.45	0.8743	309.74	-0.0009	-0.29		
C⊗	45.00	0.80	0.8974	319.20	0.8978	319.32	-0.0004	-0.12		
C⊗	45.00	0.90	0.9362	329.39	0.9362	329.42	0.0000	-0.03		
C⊗	45.00	0.99	0.9920	337.07	0.9920	337.07	0.0000	0.00		
D⊗	25.00	0.01	0.1933	25.68	0.1922	25.66	0.0011	0.02	0.0011	
D⊗	25.00	0.10	0.6178	50.62	0.6171	50.54	0.0007	0.08		0.08
D⊗	25.00	0.20	0.6840	58.80	0.6841	58.80	-0.0001	0.00		
D⊗	25.00	0.70	0.6880	58.96	0.6878	59.00	0.0002	-0.04		
D⊗	25.00	0.80	0.7232	58.44	0.7228	58.47	0.0004	-0.03		
D⊗	25.00	0.90	0.8060	55.99	0.8059	56.01	0.0001	-0.02		
D⊗	25.00	0.99	0.9715	50.27	0.9715	50.28	0.0000	0.01		
D⊗	35.00	0.01	0.2160	44.84	0.1615	41.92	0.0545	2.92	0.0545	
D⊗	35.00	0.10	0.5891	80.92	0.5712	76.45	0.0179	4.47		4.47
D⊗	35.00	0.20	0.6366	89.00	0.6474	88.92	-0.0108	0.08		
D⊗	35.00	0.30	0.6516	91.36	0.6643	91.76	-0.0127	-0.40		
D⊗	35.00	0.40	0.6588	92.26	0.6652	91.90	-0.0064	0.36		
D⊗	35.00	0.50	0.6616	92.52	0.6639	91.78	-0.0023	0.74		
D⊗	35.00	0.60	0.6638	92.62	0.6684	91.96	-0.0046	0.66		
D⊗	35.00	0.70	0.6751	92.65	0.6865	92.10	-0.0114	0.55		
D⊗	35.00	0.80	0.7147	91.54	0.7291	91.18	-0.0144	0.36		
D⊗	35.00	0.90	0.8140	86.95	0.8168	87.44	-0.0028	-0.49		
D⊗	35.00	0.99	0.9782	79.17	0.9744	79.49	0.0038	-0.32		

continued next page

Table 23 - (continued)

System	Temp. °C.	x Mole Fract.	4-Const. y Mole Fract.	4-Const. P mm. Hg.	2-Const. y Mole Fract.	2-Const. P mm. Hg.	$y_4 - y_2$ Mole Fract.	$P_4 - P_2$ mm. Hg.	Max. y Diff. Mole Fract.	Max. P Diff. mm. Hg.
D※	45.00	0.01	0.1313	65.93	0.1312	65.92	0.0001	0.01		
D※	45.00	0.10	0.5163	110.26	0.5174	110.51	-0.0009	-0.25		
D※	45.00	0.20	0.6033	127.95	0.6040	128.20	-0.0007	-0.25		-0.25
D※	45.00	0.30	0.6303	133.57	0.6299	133.59	0.0004	-0.02		
D※	45.00	0.40	0.6408	135.35	0.6395	135.21	0.0013	0.14		
D※	45.00	0.50	0.6489	136.26	0.6473	136.09	0.0016	0.17	0.0016	
D※	45.00	0.60	0.6625	137.09	0.6616	136.93	0.0009	0.16		
D※	45.00	0.70	0.6895	137.43	0.6897	137.29	-0.0002	0.14		
D※	45.00	0.80	0.7403	136.05	0.7414	135.91	-0.0011	0.14		
D※	45.00	0.90	0.8325	130.96	0.8332	130.90	-0.0007	0.06		
D※	45.00	0.99	0.9782	121.25	0.9782	121.26	0.0000	0.01		

※ system identification:

A = normal-octane--nitroethane

B = 2-methylpentane--nitroethane

C = normal-hexane--nitroethane

D = 2,2,4-trimethylpentane--nitroethane

Table 24. Values of the 4-Constant Redlich-Kister Constants at Different Temperatures

Temp. °C.	System	$(1/T) \times 10^3$ 1/°K.	A_1	A_2	A_3	A_4
25.00	A※	3.354	0.9342	- 0.0894	- 0.00641	0.00584
35.00	A※	3.245	0.8784	- 0.1042	- 0.0182	- 0.1121
45.00	A※	3.143	0.7699	- 0.0970	- 0.0099	- 0.0023
25.00	B※	3.354	0.9363	- 0.0044	- 0.0147	- 0.0084
45.00	B※	3.143	0.7059	- 0.0265	- 0.0175	0.0170

※ systems identification:

A = trimethylpentane--nitroethane

B = hexane--nitroethane

Table 25. Summary of Least Square Fit of Ternary Redlich-Kister Equation

Total No. of Constants Used in Equation	No. of Binary Constants Used	No. of Ternary Constants Calculated	Source of Binary Constants	Max. Deviation $y_{exp.} - y_{calc.}$ Mole Fract.	Max. Deviation $P_{exp.} - P_{calc.}$ mm. Hg.
12	12	0	4-constant R-K least squares fit to experimental V-L data	+ 0.002	- 0.11
13	12	1		+ 0.003	+ 0.19
14	12	2		+ 0.004	+ 0.22
15	12	3		+ 0.004	+ 0.16
6	6	0	2-constant R-K mutual solubility fit	- 0.014	+ 2.90
7	6	1		- 0.014	+ 2.45
8	6	2		- 0.013	+ 3.95
9	6	3		- 0.013	+ 3.15

System: normal octane(1)--
2,2,4-trimethylpentane(2)--
nitroethane(3)

Temperature: 35.00°C.

Table 26. Ternary Interaction Constants Obtained by Least Squares Fit to Ternary Redlich-Kister Equation

Total No. of Constants Used in Equation	No. of Ternary Constants Used	Source of Binary Constants	Value of Ternary Constants
12	0	4-constant Redlich-Kister least squares fit to experimental V-L data	----------
13	1		C = - 0.0157
14	2		C = 0.0068
14	2		D_1 = - 0.0766
15	3		C = 0.0333
15	3		D_1 = - 0.0959
15	3		D_2 = - 0.0508
6	0	2-constant Redlich-Kister mutual solubility fit	----------
7	1		C = 0.0936
8	2		C = 0.2725
8	2		D_1 = - 0.6075
9	3		C = 0.8071
9	3		D_1 = - 0.9983
9	3		D_2 = - 1.025

System: normal octane(1)--
2,2,4-trimethylpentane(2)--
nitroethane(3)

Table 27. Redlich-Kister Calculations Using the 4-Constant Least Squares Redlich-Kister Equation

x_1 Mole Fract.	y_1 Mole Fract.	P Std. mm. Hg.	γ_1	γ_2	g^E Cal./g. Mole	$-g^M$ Cal./g. Mole
0.1	0.6178	50.62	6.278	1.026	122.60	70.00
0.2	0.6840	58.81	4.079	1.107	214.83	81.65
0.3※	0.6938	60.06	2.822	1.251	277.47	84.46
0.4※	0.6882	59.54	2.079	1.475	311.62	87.13
0.5※	0.6802	59.02	1.626	1.803	318.61	92.07
0.6※	0.6776	58.91	1.346	2.270	299.95	98.81
0.7	0.6880	58.96	1.173	2.930	257.21	104.72
0.8	0.7232	58.44	1.070	3.856	191.98	104.50
0.9	0.8060	55.99	1.016	5.155	105.78	86.82

※ two-phase liquid region

Component(1): 2,2,4-trimethylpentane

Component(2): nitroethane

Temperature: 25.00°C.

0.1	0.5891	80.92	6.005	1.039	130.81	68.26
0.2	0.6366	89.00	3.619	1.134	219.22	87.21
0.3	0.6516	91.36	2.541	1.275	275.44	98.64
0.4※	0.6588	92.26	1.942	1.473	304.87	107.25
0.5※	0.6616	92.52	1.562	1.761	309.66	114.80
0.6※	0.6638	92.61	1.306	2.190	290.17	121.96
0.7	0.6751	92.65	1.140	2.819	246.52	127.55
0.8	0.7147	91.54	1.045	3.656	180.10	126.32
0.9	0.8140	86.95	1.005	4.508	95.10	103.97

※ no experimental measurements made in this concentration region

Component(1): 2,2,4-trimethylpentane

Component(2): nitroethane

Temperature: 35.00°C.

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Table 27 - (continued)

x_1 Mole Fract.	y_1 Mole Fract.	P Std. mm. Hg.	γ_1	γ_2	g^E Cal./g. Mole	$-g^M$ Cal./g. Mole
0.1	0.5163	110.26	4.660	1.023	110.35	95.17
0.2	0.6033	127.95	3.203	1.093	192.16	124.21
0.3	0.6303	133.57	2.339	1.213	246.78	139.43
0.4	0.6408	135.35	1.808	1.394	275.63	149.87
0.5	0.6489	136.26	1.473	1.647	280.19	158.04
0.6	0.6625	137.09	1.261	1.992	262.05	163.45
0.7	0.6895	137.43	1.128	2.447	222.96	163.25
0.8	0.7403	136.05	1.050	3.030	164.81	151.56
0.9	0.8325	130.96	1.011	3.746	89.71	115.82

Component(1): 2,2,4-trimethylpentane
Component(2): nitroethane
Temperature: 45.00°C.

0.1	0.3290	49.01	6.652	1.029	131.69	67.38
0.2※	0.3899	51.99	4.204	1.115	229.30	77.13
0.3※	0.3973	52.27	2.875	1.265	294.88	79.19
0.4※	0.3897	52.21	2.110	1.494	330.42	81.71
0.5※	0.3807	52.33	1.650	1.826	337.74	86.72
0.6※	0.3776	52.44	1.365	2.303	318.50	93.63
0.7※	0.3873	51.83	1.186	2.987	274.10	99.97
0.8	0.4234	49.15	1.077	3.983	205.71	100.71
0.9	0.5291	51.77	1.019	5.468	114.18	84.89

※ Two-phase liquid region
Component(1): normal octane
Component(2): nitroethane
Temperature: 35.00°C.

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Table 27 - (continued)

x_1 Mole Fract.	y_1 Mole Fract.	P Std. mm. Hg.	γ_1	γ_2	g^E Cal./g. Mole	$-g^M$ Cal./g. Mole
0.1	0.8580	135.46	5.238	1.018	107.60	85.01
0.2	0.8985	179.74	3.775	1.079	193.38	103.10
0.3	0.9085	193.91	2.779	1.195	255.57	106.36
0.4※	0.9102	196.23	2.116	1.384	293.19	105.56
0.5※	0.9091	195.09	1.678	1.673	305.86	104.83
0.6※	0.9083	194.35	1.390	2.107	293.60	105.15
0.7	0.9107	195.71	1.202	2.756	256.68	105.25
0.8	0.9206	199.67	1.085	3.746	195.39	101.09
0.9	0.9454	205.71	1.021	5.304	109.89	82.72

※ Two-phase liquid region
Component(1): 2-methylpentane
Component(2): nitroethane
Temperature: 25.00°C.

0.1	0.8220	108.20	5.700	1.020	113.71	78.90
0.2	0.8692	139.91	4.000	1.086	203.40	93.09
0.3※	0.8797	148.77	2.894	1.210	267.91	94.02
0.4※	0.8801	149.11	2.177	1.410	306.63	92.13
0.5※	0.8769	147.24	1.710	1.719	319.33	91.36
0.6※	0.8740	145.95	1.405	2.184	306.09	92.66
0.7※	0.8755	146.30	1.209	2.888	267.21	94.73
0.8	0.8873	148.32	1.087	3.968	203.03	93.45
0.9	0.9208	150.95	1.021	5.666	113.90	78.71

※ Two-phase liquid region
Component(1): normal hexane
Component(2): nitroethane
Temperature: 25.00°C.

Table 27 - (continued)

x_1 Mole Fract.	y_1 Mole Fract.	P Std. mm. Hg.	γ_1	γ_2	g^E Cal./g. Mole	$-g^M$ Cal./g. Mole
0.1	0.7151	185.96	3.787	1.015	92.64	112.88
0.2	0.7982	246.20	2.876	1.066	165.78	150.58
0.3	0.8262	273.37	2.228	1.161	217.84	168.37
0.4	0.8393	286.12	1.781	1.309	248.17	177.32
0.5	0.8482	293.88	1.479	1.524	256.89	181.34
0.6	0.8583	301.08	1.276	1.824	244.57	180.93
0.7	0.8734	309.45	1.144	2.235	212.03	174.18
0.8	0.8974	319.20	1.061	2.801	160.10	156.27
0.9	0.9362	329.39	1.015	3.598	89.38	116.15

Component(1): normal hexane

Component(2): nitroethane

Temperature: 45.00°C.

APPENDIX G

VIRIAL COEFFICIENTS

The equation of state used to describe the behavior of the gas phase for the purposes of this research is shown in Equation (23) for one mole of the gas.

$$PV = RT\left(1 + \frac{B}{V}\right) \tag{23}$$

B is the second virial coefficient. Since the virial coefficients were not available for all of the substances at the desired temperature, an arbitrary decision was made to calculate the virial coefficients of the pure components by the acentric factor method of Pitzer and Curl[23]. This method is based on a modification of the theory of corresponding states. Equation (24) presents the Pitzer and Curl[23] equation used for calculating the second virial coefficient.

$$B = \frac{RT_c}{P_c}\left[(0.1445 + 0.073\ \omega) - (0.330 - 0.46\ \omega)T_r^{-1} - (0.1385 + 0.50\ \omega)T_r^{-2} - (0.0121 + 0.097\ \omega)T_r^{-3} - 0.0073\ \omega\ T_r^{-8}\right] \tag{24}$$

where

$$\omega = -\log\left(\frac{P^o}{P_c}\right) - 1.000 \text{ at } T_r = 0.7 \tag{25}$$

For the second virial coefficient of the binary mixtures the graph presented by Fox and Lambert[24] was used. This graph was an

empirical correlation of the reduced second virial coefficient of the mixture, B_{12}/V^*_{12}, as a function of the reduced temperature, T/T^*_{12}, where

$$T^*_{12} = \left(\frac{T}{T_{c_{11}}} \quad \frac{T}{T_{c_{22}}}\right)^{1/2} \tag{26}$$

$$(V^*_{12})^{1/3} = \frac{1}{2}\left[\left(\frac{V_{11}}{V_{c_{11}}}\right)^{1/3} + \left(\frac{V_{22}}{V_{c_{22}}}\right)^{1/3}\right] \tag{27}$$

The values of ω [Equation (25)] were calculated from vapor pressure data presented in API 44[20].

Table 17 presents the values of B_{11}, B_{12}, and B_{22} for the systems used in this research at the temperatures of interest. The molal volumes and the second virial coefficients used for the nitromethane--benzene system were taken from Reference (5) in order to furnish a common basis for comparing the results of this research with that of Brown and Smith[5]. The second virial coefficients for the other systems studied in this research were calculated by the method described above. The molal volumes of the liquid and the critical constants for the hydrocarbons were taken from Reference (31). The critical constants for nitroethane were estimated by the group contribution methods reported by Reid and Sherwood[33], and are shown below:

T_c = 593°K.

P_c = 50.9 atm.

V_c = 0.230 liters/g. mole.

Table 17. Second Virial Coefficients and Liquid Molal Volumes Used for Computations for Binary Solutions

System	Temperature °C.	V_1^o ℓ/mole	V_2^o ℓ/mole	$-B_{11}$ ℓ/mole	$-B_{22}$ ℓ/mole	$-B_{12}$ ℓ/mole
2,2,4-trimethylpentane--nitroethane	25.00	0.166	0.072	2.93	2.37	1.88
2,2,4-trimethylpentane--nitroethane	35.00	0.170	0.072	2.65	2.11	1.76
2,2,4-trimethylpentane--nitroethane	45.00	0.170	0.074	2.42	1.88	1.74
normal octane--nitroethane	35.00	0.160	0.072	3.71	2.11	1.88
normal hexane--nitroethane	25.00	0.132	0.072	1.89	2.37	1.52
normal hexane--nitroethane	45.00	0.135	0.074	1.58	1.88	1.32
2-methylpentane--nitroethane	25.00	0.133	0.072	1.65	2.37	1.51
nitromethane--benzene	45.00	0.060	0.090	3.11	1.23	1.13

APPENDIX H

THERMODYNAMIC CONSISTENCY TEST

The remarks in this section will be considered to apply strictly only to binary solutions. This approach is used in order that the reader may see the simplicity of the concept involved in this consistency test. These ideas have evidently been heretofore overlooked by previous workers, probably because they appeared so simple on the surface as to create doubt as to their validity. Hence it was felt that the explanation and proof of the method for the binary case would serve the purpose of pointing out the power of the method, without any loss in generality. The reader will find that the method and the proof can be extended to multicomponent systems, after the binary mixture method and proof are understood.

It is well-known that if one measures a set of vapor-liquid equilibrium data (x, y, P, T), the data are thermodynamically consistent if and only if the appropriate form of the Gibbs-Duhem equation is satisfied identically for every (x, y, P, T) point in the set.

Now, suppose someone exhibits an algebraic function $g^E(x)_{model}$ for the molar Gibbs excess free energy which possesses the following properties:

1. $\left(\sum_i n_i\right)\left(g^E(x)_{model}\right) = G^E(x)_{model}$, the total Gibbs free energy function.

2. $g^E(x)_{model}$ is continuous for $0 \leq x \leq 1$, $x = n_1/(n_1 + n_2)$.

3. $\dfrac{\partial\{\sum_i n_i[g^E(x)_{model}]\}}{\partial n_i} = \dfrac{\partial G^E(x)_{model}}{\partial n_i}$ exists and is continuous for $0 \leq x \leq 1$.

4. The function $\left(\sum_i n_i\right)\left(g^E(x)_{model}\right) = G^E(x)_{model}$ satisfies the end conditions: $G^E(0) = G^E(1) = 0$.

Classical thermodynamics tells us that at constant T

$$G^E(P,n_1,n_2)_{thermo} = \left(\sum_i n_i\right)\left(\sum_i x_i\ \mu_i^E\right) \tag{28}$$

Equating $G^E(P,n_1,n_2)_{thermo}$ to $G^E(x)_{model}$ we obtain:

$$G^E(P,n_1,n_2)_{thermo} = \left(\sum_i n_i\right)\left(\sum_i x_i\ \mu_i^E\right) = G^E(x)_{model} \tag{29}$$

From (28) we also obtain at constant T

$$\left(\frac{dG^E(P,n_1,n_2)}{dn_1}\right)_{n_2} = \mu^E_{1\,thermo} + \sum_j \left[n_j\left(\frac{\partial \mu_j^E}{\partial n_1}\right)_{T,n_j}\right] \tag{30}$$

From (29) and (30) we obtain

$$\frac{dG^E_{model}}{dn_1} = \mu^E_{1\,thermo} + \sum_j \left[n_j\left(\frac{\partial \mu_j^E}{\partial n_1}\right)_{T,n_j}\right] \tag{31}$$

By thermodynamics we can also relate $(\mu_i^E)_{thermo}$ to a functional relationship involving (x, y, P, T); i.e., one which is evaluated from the experimental data:

$$(\mu_i^E)_{\text{thermo}} = \mu_i^E(x,y,P,T) \tag{32}$$

Substituting Equation (32) into Equation (30) we obtain for constant temperature:

$$\frac{dG^E_{\text{model}}}{dn_1} = \mu_1^E(x,y,P,T) + \sum_j \left[n_j \left(\frac{\partial \mu_j^E(x,y,P,T)}{\partial n_1} \right)_{T,n_j} \right] \tag{33}$$

Ibl and Dodge[31] showed that:

$$\sum_j \left[n_j \left(\frac{\partial \mu_j^E(x,y,P,T)}{\partial n_1} \right)_{T,n_j} \right] = \Delta V^E \left(\frac{dP}{dn_1} \right)_T \tag{34}$$

From Equations (33) and (34) we then obtain for constant temperature:

$$\left[\frac{dG^E_{\text{model}}}{dn_1} - \Delta V^E \left(\frac{dP}{dn_1} \right)_T = \mu_1^E(x,y,P,T) \right]_{\text{constant T}} \tag{35}$$

By an analogous procedure one can obtain a similar equation for constant pressure:

$$\left[\frac{dG^E_{\text{model}}}{dn_1} - \frac{\Delta H^M}{T} \left(\frac{dT}{dn_1} \right)_P = \mu_1^E(x,y,P,T) \right]_{\text{constant P}} \tag{35a}$$

Similar equations are true for any component, i:

$$\left[\frac{dG^E_{\text{model}}}{dn_i} - \Delta V^E \left(\frac{dP}{dn_i} \right)_T = \mu_i^E(x,y,P,T) \right]_{\text{constant T}} \tag{35c}$$

and

$$\left[\frac{dG^E_{\text{model}}}{dn_i} - \frac{\Delta H^M}{T} \left(\frac{dT}{dn_i} \right)_P = \mu_i^E(x,y,P,T) \right]_{\text{constant P}} \tag{35d}$$

If Equations (35) are satisfied, the set of data are thermodynamically consistent and the G^E_{model} represents the data adequately. Since Equations (35) involve functions which are in terms of the experimental quantities (x, y, P, T), it is possible to calculate a set of thermodynamically consistent (x, y, P, T) data, provided the additional quantities ΔV^E or ΔH^M are available. If ΔV^E or ΔH^M are lacking, some assumption must be made concerning the error introduced by neglecting these terms.

Insofar as Equation (35c) is concerned, for the pressure and temperature ranges of the systems studied in this research, the volume term, $\Delta V^E\left(\frac{dP}{dn_1}\right)_T$, is small when compared to the other terms of Equation (35c) and can usually be neglected [Reference (34)]. Therefore for the computations in this research, Equation (35c) was assumed to be:

$$\left[\frac{dG^E_{model}}{dn_i} = \mu_i^E(x,y,P,T)\right]_{\text{constant T}} \tag{36}$$

It is worthwhile to remember that equation (35c) was obtained by requiring the isothermal form of the Gibbs-Duhem equation [Equation (34)] to be identically true, and Equation (36) was obtained from Equation (35c) by the assumption that the term $\Delta V^E\left(\frac{dP}{dn_1}\right)_T$ was negligibly small. Thus one can conclude from Equation (36) that if one can exhibit an algebraic model, $G^E(x)_{model}$, for which Equation (36) is true at each data point of the set of (x, y, P, T) experimental data, then the data satisfy the necessary and sufficient condition for thermodynamic consistency. It should, however, be pointed out that if one exhibits an

algebraic model, $G^E(x)_{model}$, for which Equation (36) is not true for each data point of the set of (x, y, P, T) experimental data, one can only conclude that either the $G^E(x)_{model}$ does not adequately fit the experimental data, or else the data are not thermodynamically consistent, or both. Therefore the Equation (36) is a sufficient condition for thermodynamic consistency.

It should be remembered that this method is not dependent in any way on the manner in which one obtains the $g^E(x)_{model}$ function. All that is required is that the $g^E(x)_{model}$ displayed must satisfy Equation (36).

Now the advantage of this method over other methods which have been previously proposed lies in the ability to decide how inconsistent the data are. Since Equation (36) relates a function, $\mu_i^E(x, y, P, T)$ to a function $\frac{dG^E(x)_{model}}{dn_i}$, for a binary system and given values of x and T we are left with two equations in two unknowns, y and P. Hence mathematically it is possible to solve Equation (36) to find the values of y and P which correspond to a given x and T value. By picking the (x, T) values for the experimental measurements, it is possible to find a complete set of (x, y, P, T) which are thermodynamically consistent. By comparing these values with the (x, y, P, T) values which were experimentally measured, a judgement may be made concerning how inconsistent the data are. For example, if the experimental (x, y, P, T) data are reported to four significant figures, and the calculated (y, P) values corresponding to the $(x, T)_{exp.}$ values

differ only in the fourth significant figure from the experimental (y, P) values at the same $(x, T)_{exp.}$ points, one might conclude the data are consistent, even though mathematically speaking they are not rigorously consistent. In like fashion, the method allows the individual investigator to decide the question of consistency on the basis of his own accuracy requirements. The slope test and area test, which have been frequently used in the past, do not relate the deviation of the experimental (x, y, P, T) quantities to values which are experimentally accessible. Thus if the area test gives a value of 0.2 or the slope test gives some value, say 200, it is not possible to determine the corresponding errors in the experimental (x, y, P, T) data. Thus it is felt that the new method developed in this research is more easily used and is directly related to deviations in the measured (x, y, P, T) data, thereby facilitating a more realistic judgement for using the (x, y, P, T) data for future calculations.

At this stage in the discussion we will discuss the particular equations used for the isothermal thermodynamic consistency test in this research.

The model chosen for $g^E(x)$ was the Redlich-Kister model:

$$g^E(x) = \log_e(10)\ R\ T\ x_1\ x_2 \sum_{i=1}^{K} A_i(x_1 - x_2)^{i-1} \qquad (36a)$$

In this research K was taken to be equal to or less than five. The values of $\mu_1^E(x, y, P, T)$ and $\mu_2^E(x, y, P, T)$ were calculated at each data point (x, y, P, T) using Equation (37), Equation (38), and Equation (39)

$$\mu_1^E(x,y,P,T) = R\ T\ \ln\left(\frac{y_1 P}{x_1 p_1^o}\right) + (B_{11} - V_1^o)(P - p_1^o) + R_{12}\ P(y_2^2) \qquad (37)$$

$$\mu_2^E(x,y,P,T) = R\ T\ \ln\left(\frac{y_2 P}{x_2 p_2^o}\right) + (B_{22} - V_2^o)(P - p_2^o) + R_{12}\ P(y_1^2) \qquad (38)$$

$$R_{12} = 2B_{12} - B_{11} - B_{22} \qquad (39)$$

Then $\{g_i^E\}$ was calculated by Equation (40):

$$g^E(x) = x_1\mu_1^E(x,y,P,T) + x_2\ \mu_2^E(x,y,P,T) \qquad (40)$$

The values of A_i in Equation (36a) were evaluated by a least squares fit of Equation (36a) to the data set $\{g_i^E\}$.

Substituting Equations (36a), (37), (38), and (39) into Equation (34) gives Equations (41) and (42).

$$R\ T\ \ln\left(\frac{y_1 P}{x_1 p_1^o}\right) + (B_{11} - V_1^o)(P - p_1^o) + R_{12}\ P(y_2^2) = (\mu_i^E)_{model} \qquad (41)$$

$$= R\ T\ \log_e(10)\{x_2^2[A_1 + A_2(3x_1 - x_2) + A_3(5x_1 - x_2)(x_1 - x_2)$$

$$+ A_4(7x_1 - x_2)(x_1 - x_2)^2 + A_5(9x_1 - x_2)(x_1 - x_2)^3]\}$$

$$R\ T\ \ln\left(\frac{y_2 P}{x_2 p_2^o}\right) + (B_{22} - V_2^o)(P - p_2^o) + R_{12}\ P(y_1^2) = (\mu_2^E)_{model} \qquad (42)$$

$$= R\ T\ \log_e(10)\{x_1^2[A_1 + A_2(x_1 - 3x_2) + A_3(x_1 - 5x_2)(x_1 - x_2)$$

$$+ A_4(x_1 - 7x_2)(x_1 - x_2)^2 + A_5(x_1 - 9x_2)(x_1 - x_2)^3]\}$$

Subtracting Equation (42) from Equation (41) and rearranging gives Equation (43):

$$P = \frac{[(\mu_1^E)_{model} - (\mu_2^E)_{model}] - R\ T\ \ln\left(\frac{y_1 p_2^o x_2}{y_2 p_1^o x_1}\right) - (B_{22} - V_2^o) p_2^o + (B_{11} - V_1^o) p_1^o}{(B_{11} - V_1^o - B_{22} + V_2^o + R_{12}\ y_2^2 - R_{12}\ y_1^2)} \quad (43)$$

The procedure consisted of the following:

1. Pick $(x_i)_{exp.}$, recalling that T is known (isothermal data), and assume a value for y.

2. Calculate P from Equation (43).

3. With these (x, y, P, T) values, see whether Equation (41) is satisfied.

4. If Equation (41) is true, stop; the (x, y, P, T) values are correct.

5. If Equation (41) is false, increase y by some specified increment and repeat steps 2 - 5 until 4 is true. By this procedure it was possible to generate the set of thermodynamically consistent data which satisfied both Equation (41) and Equation (42) simultaneously.

6. The set of (x, y, P, T) data were compared with the experimental data to see whether the model values and the experimental data agreed. If the data set calculated from the model agreed with the experimental data set, within the limits of the experimental error (± 0.0005 mole fraction, ± 0.05 mm. Hg.), the data were considered consistent and the particular model was said to represent the data

adequately. In general, for the systems studied in this research, more than two constants were required in the Redlich-Kister equation, and sometimes four constants were necessary. The use of five constants did not enhance the apparent consistency of the data when compared to the four-constant results for the systems studied in this research.

BIBLIOGRAPHY

1. Redlich, O., and Kister, A. T., "Thermodynamics of Nonelectrolyte Solutions," Industrial and Engineering Chemistry, 40, 345 (1948).

2. Redlich, O., Kister, A. T., and Turnquist, C. E., "Thermodynamics of Solutions. Analysis of Vapor-Liquid Equilibria," Chemical Engineering Progress, Symposium Series, 48, No. 2. 49 (1950).

3. Techo, Robert, Liquid-Liquid Phase Equilibria, unpublished Ph. D. thesis, Georgia Institute of Technology (1961).

4. Hwa, S. C. P., Phase Equilibria in Nitroparaffin-Hydrocarbon Systems, unpublished M. S. thesis, Georgia Institute of Technology (1959).

5. Brown, I., and Smith, F., "Liquid-Vapor Equilibria. VII. The Systems Nitromethane + Benzene and Nitromethane + Carbon Tetrachloride at 45°C.," Australian Journal of Chemistry, 8, 501 (1955).

6. Vilim, O., Hala, E., Fried, V., and Pick, J., "Das Gleichgewicht Flussigkeit--Dampf VIII., "Collection of Czechoslovakian Chemical Communications, 19, 1330 (1954).

7. Cantoni, A., and Feldman, J., "Vapor-Liquid Equilibria: Binary System Nitromethane--Nitroethane at Subatmospheric Pressure," Industrial and Engineering Chemistry, 45, 2580 (1953).

8. Williams, F. E., "A Binary Mixture for Evaluating Low Pressure Distillation Columns," Industrial and Engineering Chemistry, 39, 779 (1947).

9. Robinson, C. S., and Gilliland, E. R., Elements of Fractional Distillation, McGraw-Hill Book Company, New York (1950) 98.

10. Treybal, R. E., Liquid Extraction, McGraw-Hill Book Company, Inc., New York (1951) 59 ff.

11. Rowlinson, J. S., Liquids and Liquid Mixtures, Academic Press, Inc., New York (1959) 111-112.

12. Herington, E. F. G., "New Methods for the Interpolation of Ternary Vapor-Liquid Data," Journal of Applied Chemistry (London), 2, 11 (1952).

13. Mertes, T. S., and Colburn, A. P., "Binary Mixtures of n-Butane, Isobutane, and 1-Butene with Furfural," Industrial and Engineering Chemistry, 39, 787 (1947).

14. Rall, W., and Schäfer, K., "Thermodynamische Untersuchungen an flüssigen Mischsystemen von Aceton und n-Pentane sowie von Aceton und n-Hexan," Zeitschrift für Elektrochemie, 63, 1019 (1959).

15. Severns, W. H., Sesonske, A., Perry, R. H., and Pigford, R. L., "Estimation of Ternary Vapor-Liquid Data," American Institute of Chemical Engineers Journal, 1, 401 (1955).

16. Hala, E., Pick, J., Fried, V., and Vilim, O., Vapor-Liquid Equilibrium, Pergamon Press, New York (1958).

17. Brombacher, W. G., Johnson, D. P., and Cross, J. L., Mercury Barometers and Manometers, National Bureau of Standards Monograph 8, U. S. Government Printing Office, Washington, D. C. (1960).

18. Scatchard, G., and Raymond, C. L., "Vapor-Liquid Equilibrium II Chloroform - Ethanol Mixtures at 35, 45, and 55°," Journal of the American Chemical Society, 60, 1278 (1938).

19. Hengstebeck, R. J., Distillation Principles and Design Procedures, Reinhold Publishing Company, New York (1961).

20. Rossini, F. D., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh (1953).

21. Toops, Emory E., Jr., "Physical Properties of Eight High-Purity Nitroparaffins," Journal of Physical Chemistry, 60, 304 (1956).

22. Prigogine, I., and Defay, R., Chemical Thermodynamics, Translated by Everett, D. H., Volume I, Longmans, Green and Company, Inc., London (1954).

23. Pitzer, K. S., and Curl, R. F., Jr., "The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient," Journal of the American Chemical Society, 79, 2369 (1957).

24. Fox, J. H. P., and Lambert, J. D., "The Second Virial Coefficients of Mixed Organic Vapours," Proceedings of the Royal Society (London), A210, 557 (1951).

25. Hala, E., Fried, V., Pick, J., and Vilim, O., "Das Gleichgewicht Flussigkeit--Dampf IV.," Collection Czechoslovakian Chemical Communications, 19, 16 (1954).

26. Carlson, H. C., and Colburn, A. P., "Utilization of Theoretical Methods to Extend Data," Industrial and Engineering Chemistry, 34, 581 (1942).

27. Benedict, M., Johnson, D. A., Solomon, E., and Rubin, L. C., "Extractive and Azeotropic Distillation," Transactions of the American Institute of Chemical Engineers, 41, 371 (1945).

28. Wohl. K., "Thermodynamic Evaluation of Binary and Ternary Liquid Systems," Transactions of the American Institute of Chemical Engineers, 42, 215 (1946).

29. Scatchard, G., "Solutions of Nonelectrolytes," Annual Review of Physical Chemistry, 3, 269 (1952).

30. Margules, M., "Ueber die Zusammensetzung der gesaettigten Daempfe von Mischungen," Anzeigen der Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, 104, 1243 (1895).

31. Ibl, N. V., and Dodge, B. F., "Note on the Duhem Equation," Chemical Engineering Science, 2, 120 (1953).

32. Keulemans, A. I. M., Gas Chromatography, Reinhold Publishing Corporation, New York (1957) 31 ff.

33. Reid, R. C., and Sherwood, T. K., The Properties of Gases and Liquids, McGraw-Hill Book Company (1958) Chapter II.

34. Denbigh, K., The Principles of Chemical Equilibrium, Cambridge University Press, Cambridge (1957) 231.

VITA

James Byrd Edwards, II, born October 11, 1933, in New Orleans, Louisiana, was the youngest of the four children born to Dr. Robert Crawford Edwards and Annadawn Watson Edwards.

He completed his high school education at Jackson High School, Jackson, Georgia, where he was graduated as valedictorian. He was awarded the degree of Bachelor of Chemical Engineering (Co-op) from the Georgia Institute of Technology in 1955. His Cooperative Plan employer was Law Laboratories, Atlanta, Georgia.

In 1955 he was employed as a Process Development Engineer at the Procter and Gamble Company in Cincinnati, Ohio. In 1958, he enrolled in the Graduate Division of the Georgia Institute of Technology to begin work in the School of Chemical Engineering on the degree of Doctor of Philosophy.

He was awarded the Shell Chemical Company Fellowship for three consecutive academic years beginning with 1958-1959. He served for four years on the Dean of Students Staff as a Resident Advisor. During the summer of 1959, he served on the teaching staff of the Chemical Engineering Department, and during 1961-1962 he was a member of the teaching staff of the Mathematics Department. He has been employed by the Rich Electronic Computer Center from June 1961 to the present. Part of this employment was supported by a grant from the National Science Foundation through the Rich Electronic Computer Center and

involved a study of the computer aspects of vapor-liquid and liquid-liquid equilibrium computations.

He is a member of the Society of the Sigma Xi, the American Institute of Chemical Engineers, and the Association for Computing Machinery.